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CHLORINE DECAY IN A LARGE RIVER

BY

GREGORY D. MILNE ©

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The undersigned certify that they have read, and recommend to the Faculty of Graduate Studies and Research for acceptance, a thesis entitled **Chlorine Decay in a Large River** submitted by **Gregory D. Milne** in partial fulfillment of the requirements for the degree of **Master of Science** in **Environmental Engineering**.

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Abstract

The study reported herein involved field investigations of the mixing and decay of chlorinated discharges from two water treatment plants in the City of Edmonton, Canada. To destroy microorganisms of public health concern, both of these plants utilize chlorine as a final disinfectant. A portion of the product water is used in the treatment process, and is then discharged into the North Saskatchewan River. The discharge of these waters may result in negative impacts within the receiving stream. These impacts are dependent on the concentration of residual chlorine present, which is a function of the rate of decay of chlorine,and the mixing properties of the river. Current understanding of the rate of chlorine decay within the environment is limitted. Several laboratory investigations have been conducted, but these do not adequately simulate the site-specific conditions of the receiving stream. To obtain accurate estimates of chlorine decay rates, field investigations are required.

Field studies investigating the in-stream rate of decay of residual chlorine were conducted in the North Saskatchewan River. Field data was obtained by monitoring downstream concentration profiles of residual chlorine resulting from a steady-state discharge from the water treatment plants. Due to the large size of the North Saskatchewan, the discharge plume does not mix competely with the river, and significant transverse concentration gradients exist for a considerable distance downstream. Within this region, dilution of the plume must be considered . The mixing behavior of the discharge downstream from the water treatment plant outfalls was determined by conducting tracer studies using Rhodamine WT dye. Using a two-dimensional mixing model, the effects of dilution on the dye plume were determined. Subsequent application of the model, with a decay term included, enabled determination of the gross-rate of chlorine decay within the river. Field decay rates were similar to those reported by other investigators, and were substantially greater than what would be predicted from laboratory studies.

Preliminary investigations into the dominant decay mechanisms were also conducted using plume data supplemented by additional laboratory and field investigations. Rate constants for water column chlorine demand, benthic demand, and photolytic degradation were determined. Results indicate that benthic demand may represent the predominant sink for residual chlorine within the North Saskatchewan River.

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Table of Contents

1.0 Introduction 1
  1.1 Background 1
  1.2 Scope of Investigation 2

2.0 Review of Literature 4
  2.1 Chlorine Chemistry in Freshwaters 4
    2.1.1 Aqueous Chlorine Speciation 5
    2.1.2 Chlorine Fate and Decay in Natural Waters 10
      2.1.2.1 Chemical Decomposition 11
      2.1.2.2 Water Column Chlorine Demand 16
      2.1.2.3 Adsorption to Sediments 17
      2.1.2.4 Benthic Demand 18
      2.1.2.5 Volatilization 19
      2.1.2.6 Photolysis 21
      2.1.2.7 Temperature effects 22
  2.2 River Mixing 23
    2.2.1 Transverse Mixing Theory 23
    2.2.2 The Transverse Mixing Coefficient 26
  2.3 Effluent Discharge Modelling 29
    2.3.1 Available models 29
    2.3.2 TRSMIX 29
  2.4 Environmental Impacts of Chlorinated Discharges 30
  2.5 In-stream Chlorine Standards and Guidelines 31

3.0 Research Objectives 33
  3.1 Problem Overview 33
  3.2 Specific Objectives 33

4.0 Methods and Materials 35
  4.1 Field Investigations 35
    4.1.1 Field Surveys 35
    4.1.2 Tracer Study Methods 37
      4.1.2.1 Injection 37
      4.1.2.2 Sample Collection 39
      4.1.2.3 Rhodamine WT Analysis 42

4.1.3 Chlorine Study Methods 42
    4.1.3.1 Discharge Conditions 43
    4.1.3.2 Sample Collection 43
    4.1.3.2 Chlorine Analysis 43
4.1.4 Bacteriological Methods 46
4.1.4 Benthic Chlorine Demand 46
4.2 Laboratory Investigations of Chlorine Decay 50

5.0 Site Description 55
5.1 General 55
5.2 Rossdale Water Treatment Plant 57
5.3 North Saskatchewan River at Rossdale Water Treatment Plant 58
5.4 E.L. Smith Water Treatment Plant 62
5.5 North Saskatchewan River at E.L. Smith Water Treatment Plant 62

6.0 Results

6.1 Rossdale Water Treatment Plant Field Study 66
  6.1.1 Rhodamine WT Tracer Test 66
    6.1.1.1 Mass Balance Analysis 70
    6.1.1.2 Transverse Mixing Coefficient Determination 74
  6.1.2 Residual Chlorine Surveys 76
    6.1.2.1 Chlorine Mass Balance Analysis 83
    6.1.2.2 Decay Coefficient Determination 83
  6.1.3 Microbiological Study 87
6.2 E.L. Smith Water Treatment Plant Field Study 91
  6.2.1 Rhodamine WT Tracer Test 91
    6.2.1.1 Mass Balance Analysis 96
    6.2.1.2 Transverse Mixing Coefficient Determination 98
  6.2.2 Residual Chlorine Surveys 99
    6.2.2.1 Chlorine Survey Results 99
    6.2.2.2 Decay Coefficient Determination 99
  6.2.3 Microbiological Tests 108
  6.2.4 Benthic Chlorine Demand Study 112
6.3 Laboratory Investigations of Water Column Chlorine Demand 117

7.0 Discussion 119
  7.1 Transverse Mixing 119
  7.2 Chlorine Decay 124
    7.2.1 Gross Rate of Chlorine Decay 124
    7.2.2 Chlorine Decay Pathways 128
      7.2.2.1 Water Column Chlorine Decay 128
      7.2.2.2 Photolytic Chlorine Decay 129
      7.2.2.3 Benthic Chlorine Demand 133
      7.2.2.4 Chlorine Volatilization 135

8.0 Summary and Conclusions 140

9.0 Recommendations for Future Work 142

10.0 References Cited 143

Appendix A Cross-sectional geometry and flow distribution plots 154
Appendix B Rhodamine WT tracer study permits 167
Appendix C Rhodamine WT tracer data 176
Appendix D Fluorometer calibration plot 180
Appendix E Residual chlorine data 182
Appendix F Chlorine plume microbial data 188

List of Tables

Table 2.1 Literature survey of reported first-order decay coefficients 12
Table 4.1 Summary of temporary and permanent benchmarks 36
Table 4.2 Dye discharge conditions 40
Table 4.3 Dye sample collection points 40
Table 4.4 Chlorinated water discharge conditions 44
Table 4.5 Chlorine sample collection points 44
Table 4.6 Microbial sample collection points 49
Table 5.1 Hydraulic properties of North Saskatchewan River downstream of Rossdale Water Treatment Plant (September 4, 1990) 61
Table 5.2 Hydraulic properties of North Saskatchewan River downstream of E.L. Smith Water Treatment Plant (September 25, 1990) 65
Table 6.1 Rhodamine WT tracer mass balance 73
Table 6.2 Transverse mixing coefficients β and E_z 77
Table 6.3 Analysis of Rossdale Plant 3 water quality parameters 80
Table 6.4 Rhodamine WT tracer mass balance 97
Table 6.5 Transverse mixing coefficients β and E_z 102
Table 6.6 Analysis of Rossdale Plant 3 water quality parameters (September 26, 1990) 103
Table 7.1 Tracer plume and river characteristics downstream of Rossdale Water Treatment Plant (September 5, 1990) 122
Table 7.2 Tracer plume and river characteristics downstream of E.L. Smith Water Treatment Plant (September 25, 1990) 122
Table 7.3 Paired t-test examining the effects of photolysis on chlorine decay in the E.L. Smith plume 132
Table C1 Rhodamine WT tracer data from Rossdale field tests 170
Table C2 Rhodamine WT tracer data from E.L. Smith field tests 171
Table E1 Chlorine residual data from Rossdale plume 176
Table E2 Chlorine residual data from E.L. Smith plume 178
Table F1 Microbial data from Rossdale chlorine plume 182
Table F2 Microbial data from E.L. Smith chlorine plume 183

List of Figures

Figure 2.1 Possible reaction pathways for chlorine in natural waters 8
Figure 4.1 Rhodamine WT tracer injection system 38
Figure 4.2 Rhodamine WT plume immediately downstream of the E.L. Smith Water Treatment Plant 41
Figure 4.3 Field operation of amperometric titrators 47
Figure 4.4 In-stream chlorine analysis downstream from the E.L. Smith Water Treatment Plant 48
Figure 4.5 Benthic uptake apparatus 51
Figure 4.6 Sampling of the benthic uptake chamber 52
Figure 4.7 Chlorine decay reaction tube 53
Figure 5.1 North Saskatchewan River upstream of Edmonton 56
Figure 5.2 Site diagram of the Rossdale Water Treatment Plant 59
Figure 5.3 Aerial photo of the North Saskatchewan River downstream from the Rossdale Water Treatment Plant (1:25000) 60
Figure 5.4 Site diagram of the E.L. Smith Water Treatment Plant 63
Figure 5.5 Aerial photo of the North Saskatchewan River downstream from the E.L. Smith Water Treatment Plant (1:25000) 64
Figure 6.1a Rhodamine WT tracer profile: Rossdale cross sections 1 to 3 67
Figure 6.1b Rhodamine WT tracer profile: Rossdale cross sections 4 to 6 67
Figure 6.2a Dimensionless tracer profile: Rossdale cross section 1 68
Figure 6.2c Dimensionless tracer profile: Rossdale cross sections 2 and 3 68
Figure 6.2c Dimensionless tracer profile: Rossdale cross sections 4 to 6 69
Figure 6.3 Velocity - depth correlation for discrete locations vs. mean channel properties 71
Figure 6.4a Model fit vs. observed tracer distribution: Rossdale cross section 3 78
Figure 6.4b Model fit vs. observed tracer distribution Rossdale cross section 4 78
Figure 6.4c Model fit vs. observed tracer distribution Rossdale cross section 5 79
Figure 6.4d Model fit vs. observed tracer distribution Rossdale cross section 6 79
Figure 6.5 Residual chlorine profiles Rossdale cross sections 1 to 3 81

Figure 6.6 Dimensionless chlorine profiles Rossdale cross sections 1 to 3 82
Figure 6.7 Chlorine flux vs. residence time (based on mean plume velocity) 84
Figure 6.8 Model predictions of TRC distribution at Rossdale cross section 3 for various decay coefficients 86
Figure 6.9a Total heterotroph distribution in the Rossdale chlorine plume 88
Figure 6.9b Total coliform distribution in the Rossdale chlorine plume 89
Figure 6.9 Fecal coliform distribution in the Rossdale chlorine plume 90
Figure 6.10a Rhodamine WT tracer profile: E.L. Smith cross section 1 92
Figure 6.10b Rhodamine WT tracer profile: E.L. Smith cross sections 2 and 3 92
Figure 6.10c Rhodamine WT tracer profile: E.L. Smith cross sections 4 to 6 93
Figure 6.11a Dimensionless tracer profile: E.L. Smith cross section 1 94
Figure 6.11b Dimensionless tracer profile: E.L. Smith cross sections 2 and 3 94
Figure 6.11c Dimensionless tracer profile: E.L. Smith cross sections 4 to 6 95
Figure 6.12a Model fit vs. observed tracer distribution: E.L.Smith cross section 3 99
Figure 6.12b Model fit vs. observed tracer distribution: E.L.Smith cross section 4 99
Figure 6.12c Model fit vs. observed tracer distribution: E.L.Smith cross section 5 100
Figure 6.12d Model fit vs. observed tracer distribution: E.L.Smith cross section 6 100
Figure 6.13 Residual chlorine profiles: E.L. Smith cross sections 1 to 4 104
Figure 6.14 Dimensionless chlorine profiles: E.L. Smith cross sections 1 to 4 105
Figure 6.15 Model predictions of TRC distribution at E.L. Smith cross section 3 for various decay coefficients 107
Figure 6.16a Total heterotroph distribution in the E.L. Smith chlorine plume 109
Figure 6.16b Total coliform distribution in the E.L. Smith chlorine plume 110
Figure 6.16c Fecal coliform distribution in the E.L. Smith chlorine plume 111
Figure 6.17 TRC consumption by benthic chlorine demand: October, 1990 114
Figure 6.18 TRC consumption by benthic chlorine demand: July, 1991 115
Figure 6.19 Water column chlorine demand, North Saskatchewan River water 118
Figure 7.1 Comparison of day-time and night-time residual chlorine concentrations in the E.L. Smith plume 130

Figure 7.2 Dimensionless comparison of day and night-time residual chlorine profiles in the E.L. Smith plume 131
Figure 7.3 Predicted fully-mixed downstream concentrations of TRC in the North Saskatchewan River using volatilization model of Rathbun (1990) 138
Figure A1 Cross sectional geometry and flow distribution: Rossdale cross section 1 155
Figure A2 Cross sectional geometry and flow distribution: Rossdale cross section 2 156
Figure A3 Cross sectional geometry and flow distribution: Rossdale cross section 3 157
Figure A4 Cross sectional geometry and flow distribution: Rossdale cross section 4 158
Figure A5 Cross sectional geometry and flow distribution: Rossdale cross section 5 159
Figure A6 Cross sectional geometry and flow distribution: Rossdale cross section 6 160
Figure A7 Cross sectional geometry and flow distribution: E.L. Smith cross section 1 161
Figure A8 Cross sectional geometry and flow distribution: E.L. Smith cross section 2 162
Figure A9 Cross sectional geometry and flow distribution: E.L. Smith cross section 3 163
Figure A10 Cross sectional geometry and flow distribution: E.L. Smith cross section 4 164
Figure A11 Cross sectional geometry and flow distribution: E.L. Smith cross section 5 165
Figure A12 Cross sectional geometry and flow distribution: E.L. Smith cross section 6 166
Figure D1 Fluorometer calibration plot 177

List of Symbols

a	Manning resistance coefficient
$\bar{b}$	half-plume width (m)
B	mean channel width (m)
C	concentration ($\mu g\ L^{-1}$, $mg\ L^{-1}$)
C_a	aqueous phase concentration ($\mu g\ L^{-1}$, $mg\ L^{-1}$)
C_o	initial concentration ($\mu g\ L^{-1}$, $mg\ L^{-1}$)
C'	dimensionless concentration
C_∞	fully-mixed concentration ($\mu g\ L^{-1}$, $mg\ L^{-1}$)
D_{50}, D_{65}, D_{90}	sieve sizes at which 50, 65 and 90% of particles are finer by weight (mm)
E_z	transverse mixing coefficient ($m^2\ s^{-1}$)
h	local stream depth (m)
H	mean cross-sectional depth (m)
k	first-order decay rate coefficient (d^{-1})
k_G	gas-film mass-transfer coefficient ($m\ d^{-1}$)
k_L	liquid-film mass-transfer coefficient ($m\ d^{-1}$)
k_p	first-order decay rate constant due to photolysis (d^{-1})
k_v	first-order decay rate constant due to volatalization (d^{-1})
K_{OL}	over-all mass-transfer coefficient for volatalization ($m\ d^{-1}$)
K_2	stream reaeration coefficient (d^{-1})
l	general length scale (m)
N	titrant normality ($eq\ mol^{-1}$)
q	cumulative discharge from left bank ($m^3\ s^{-1}$)
Q	river discharge ($m^3\ s^{-1}$)
R	universal gas constant ($kPa\ M^3\ g^{-1}\ mol^{-1}$)
$s_{\bar{y}}$	standard deviation
t	time (s, d)
t	Student-t statistic
T	temperature (°C, K)
u_*	shear velocity ($m\ s^{-1}$)
uh^2E_z	local diffusion factor ($m^5\ s^{-2}$)
u, v, w	local velocity components in the x, y, and z directions ($m\ s^{-1}$)
U, V, W	mean velocity components in the x, y, and z directions ($m\ s^{-1}$)
V_t	titrant volume (mL)
x_m	distance for complete transverse mixing (m)

x_v	distance for complete vertical mixing (m)
$\bar{x}$	mean value
Y	mean stream depth (m)
β	dimensionless mixing coefficient
Δx	longitudinal grid spacing (m)
$\Delta \eta$	dimensionless transverse grid spacing
ε_x, ε_y, ε_z	turbulent diffusion coefficients in the x, y, and z directions (m^2/s)
η	dimensionless discharge
θ	vant't - Hoff Arrhenius constant
ν	degrees of freedom

1.0 Introduction

1.1 Background

This research focused upon the processes governing the in-stream decay and mixing of chlorinated discharges from water treatment plants in the City of Edmonton, Canada. Chlorinated process waters from routine filter backwash procedures and from emergency plant by-pass operations are currently discharged into the North Saskatchewan River from the Rossdale and E.L. Smith Water Treatment Plants. These effluents are discharged untreated containing total residual chlorine concentrations up to 2.0 mg/L, presenting a situation by which adverse impacts on the receiving environment could result.

Stanley and Smith (1991) completed a preliminary assessment of residual chlorine distribution and impacts in and downstream of the water treatment plants and concluded that limits of 0.002 mg/L total residual chlorine (TRC) proposed by Alberta Environment may be exceeded along the boundaries of the mixing zone. However, this study was limited due to the uncertainty associated with parameters used to describe chlorine decay and river mixing processes. They selected conservative values from the literature to account for a lack of field measurements, but expressed uncertainty in the use of literature decay rates due to the large range of reported values.

The field of chlorination chemistry, especially as applied to water treatment applications, has been the subject of intensive study. As a result of concerns about the health effects of chlorination by-products, and engineering requirements to maximize the efficient application of chlorine, a substantial volume of literature on chlorine reactions has been published. However, the very quality that makes chlorine such a valuable tool in the water treatment process, its high oxidation potential, severely complicates prediction of it's behaviour in the natural environment.

While the knowledge of chlorine chemistry within the relatively controlled environment of laboratory and water treatment applications may be approaching a satisfactory level, a comparable level of understanding of it's behaviour following discharge into the environment has not yet been achieved. Several researchers have attempted to quantify rates of chlorine decay in the environment through laboratory studies, but adequate bench scale simulation of the numerous physical and chemical processes by which residual chlorine can be depleted within a stream is extremely difficult.

Few attempts to determine the fate of residual chlorine discharges have been conducted in the field. The studies that have been reported undoubtedly provide more accurate estimates of in-stream decay rates than those obtained from a laboratory setting. Although the chemical and physical processes within the stream are accurately simulated in these tests, these studies have usually been conducted on small streams~~,~~ where transverse mixing occurred very rapidly. In these studies, a simplified consideration of the mixing behaviour of the stream was often sufficient. However, for the study reported herein, which occurs in a relatively large river, the mixing between the discharge plume and the main body of flow could not be ignored.

The primary objective of this study was to determine the rate of decay of residual chlorine within the North Saskatchewan River from discharges arising from the City of Edmonton's two water treatment plants. Due to the large size of the North Saskatchewan River, the assumption of a completely mixed effluent is invalid. To adequately determine the rate of chlorine decay, a thorough understanding of the mixing behaviour of the discharge plumes was required. This was achieved by conducting dye tracer tests downstream from each water treatment plant. Site-specific values for the mixing coefficients were determined by analysis of the tracer data with the numerical mixing model TRSMIX. Field investigations of the in-stream distribution of residual chlorine resulting from steady-state discharges from the water treatment plants were conducted to provide data on chlorine distribution and decay. Subsequent analysis of the in-stream chlorine data using the TRSMIX model allowed for separation of the dilution process from the processes governing chlorine decay, and enabled determination of the in-stream decay rate coefficient. Additional bench scale laboratory and field investigations were performed to obtain order-of-magnitude estimates of the contributions of the individual chlorine removal pathways to the gross rate of chlorine decay.

1.2 Scope of Investigation

This research was undertaken to obtain an improved understanding of the environmental behaviour of residual chlorine in water treatment plant effluents discharged to a receiving water body. Field investigations were used to determine the rate of chlorine decay within the effluent plume. Supplemental laboratory studies, and limited in-situ investigations were also performed to supplement, and to better define the information gained from the field investigations. Due the the highly variable water quality within the receiving stream, an exhaustive investigation under all possible water quality conditions was not feasible. The intent of this project was to improve estimates of the site-specific decay parameters from the order-of-magnitude approximations available from the literature, and to improve knowledge of the decay mechanisms such that the impact of various stream conditions on the overall rate of chlorine decay could be predicted.

The North Saskatchewan River is a relatively large river, with varied and complex hydrography. It is subject to considerable discharge extremes, and the entire 'character' of the flow changes on a seasonal basis. Through the City of Edmonton, some portions may be ice-covered throughout the winter, whereas other sections remain open year round. Due to the wide range of possible flow conditions and water quality, it was beyond the scope of this project to investigate chlorine decay under all the possible conditions. However, by supplementing the field plume studies with information obtained from more controlled and limited laboratory investigations, an improved understanding of the behaviour of chlorinated discharges within the North Saskatchewan could be obtained.

2.0 Review of Literature

A considerable body of research studying the fate and behaviour of pollutant discharges is available within the scientific literature. For the specific case of water treatment plant discharges of residual chlorine, the primary processes responsible for the reduction of total residual chlorine (TRC) concentrations within the environment are the chemical decay of TRC and mixing and dilution within the receiving stream. Although discharges of TRC can represent a significant environmental problem, little information on the behaviour of these discharges specific to water treatment plants is available. Relevant information on TRC speciation, persistence and toxicology extracted from studies of chlorinated wastewater treatment plant and cooling water discharges, along with a discussion of river mixing processes are summarized below.

2.1 Chlorine Chemistry in Freshwaters

To assess the environmental impact of residual chlorine on the receiving environment, it is necessary to adequately understand the behaviour of chlorine within natural freshwaters. Following discharge into natural waters, chlorine can exist in molecular form, and is also found combined with other naturally occurring organic and inorganic constituents. The chemical and toxicological properties of these effluents is a function not only of the quantity and concentration of chlorine discharged, but also of the form in which it exists. Many water quality factors influence aqueous chlorine speciation, including temperature, pH, the types and concentrations of organic and inorganic constituents, and other in-stream processes. An understanding of these processes is necessary to accurately assess potential environmental impacts, and for the establishment of realistic guidelines and standards. This review will briefly describe chlorine behaviour in freshwaters and will summarize the current state of knowledge. However, the subject of aqueous chlorine chemistry is vast, and several excellent summaries which should be consulted for more detailed reference are available in the literature (Jolley and Carpenter, 1983; Pierce, 1978; Jolley et al., 1975; White, 1986). Excluded from this review is chlorine chemistry in marine waters, where the presence of bromide greatly alters the chemical behaviour of chlorine.

The processes by which residual chlorine is removed from aqueous systems are complex and not well understood. The decay of chlorine within the receiving stream is a time-dependent reaction within the effluent plume resulting from chemical reactions and other physical and biochemical processes. Reactions with organic and inorganic materials present in the water, adsorption to suspended sediments, interactions with the benthic layer, volatilization, and photolysis are all mechanisms that can promote the reduction of chlorine residuals. Present understanding of these processes are very limited, and most past attempts at predicting rates of chlorine removal from natural systems have treated chlorine decay as a gross process, without detailed consideration of the numerous reaction pathways. Recent research has begun to more closely analyze the individual contributions of the above mechanisms.

2.1.1 Aqueous Chlorine Speciation

Chlorine present in aqueous solution as hypochlorous acid and hypochlorite ion is termed free chlorine (free residual chlorine, free available chlorine), while chlorine present as chloramines and organic N-chloro-compounds in which the chlorine containing compound has a lower oxidation potential than free chlorine is known as combined chlorine. The sum of these two groups is termed total residual chlorine (TRC) or combined residual chlorine (CRC). The relative amounts and speciation of free and combined chlorine is dependent upon many factors including the ratio of chlorine to ammonia nitrogen, organic nitrogen, temperature, pH, and alkalinity.

In water treatment applications, chlorine is usually applied either as chlorine gas (Cl_2) or as sodium hypochlorite (NaOCl). Elemental chlorine has a high tendency to undergo reduction from an oxidation state of zero to an oxidation state of -1. Therefore, in aqueous solutions, chlorine gas hydrolyses to form hypochlorous acid and chloride.

$$Cl_2 + 2H_2 0 \rightleftharpoons H_3 0^+ + Cl^- + HOCl^+ \qquad (2.1)$$

The hydrolysis constants for this reaction range from 1.5×10^{-4} at 0 °C to 4.0×10^{-4} at 25 °C (Jolley and Carpenter, 1983). The forward reaction rate constant has been reported as 13.7 s^{-1} at 25 °C, which suggests a half-life for molecular chlorine of 0.05 s (Jolley and Carpenter, 1983). Under conditions normally found in natural systems, this hydrolysis is therefore essentially complete at pH > 6.

In turn, HOCl, which is a weak acid, establishes an equilibrium between its dissociated and molecular forms:

$$HOCl + H_2 0 \rightleftharpoons H_3 0^+ + OCl^- \quad pKa= 7.5 \qquad (2.2)$$

Dissociation constants of 1.6 x 10^{-8} at 0 °C to 3.2 x 10^{-8} at 25 °C have been reported (Jolley and Carpenter, 1983). This reaction is rapid and is essentially at equilibrium in less than a second. This equilibrium is very important for disinfection purposes, as hypochlorous acid is a much stronger bacteriocidal agent.

In the presence of ammonia, as either NH_3 or the ammonium ion NH_4^+, or in water containing organic amines, free chlorine will combine with ammonia to form monochloramine,

$$NH_3 + HOCl \rightleftharpoons NH_2Cl + H_2O \tag{2.3}$$

dichloramine,

$$NH_3 + 2HOCl \rightleftharpoons NHCl_2 + 2H_2O \tag{2.4}$$

or

$$NH_2Cl + HOCl \rightleftharpoons NHCl_2 + H_2O \tag{2.5}$$

or trichloramine,

$$NH_3 + 3HOCl \rightleftharpoons NCl_3 + 3H_2O \tag{2.6}$$

or

$$NH_2Cl + 2HOCl \rightleftharpoons NCl_3 + 2\,H_2O \tag{2.7}$$

or

$$NHCl_2 + HOCl \rightleftharpoons NCl_3 + H_2O. \tag{2.8}$$

The exact mechanisms of the reactions between ammonia and chlorine are not fully understood. Both hypochlorous acid and ammonia participate in acid-base equilibria reactions and chloramine formation can result from reactions between neutral species, ionic species, or combinations of both. The reaction products formed are dependent upon the relative concentrations of hypochlorous acid and ammonia, the reaction time, pH, and temperature (Jolley and Carpenter, 1983). Monochloramine is typically the predominant chloramine observed at pH > 8 and when the molar ratio of hypochlorous acid to ammonia is less than 1. At lower pH or higher $HOCl:NH_3$ ratios, dichloramine and trichloramine may also be present at significant concentrations.

The rate of formation of monochloramine is rapid under normal water treatment conditions, with the reaction being approximately 90% complete in less than a minute (Jolley and Carpenter, 1983). The reaction rate constant for the formation of monochloramine from the neutral reactant species is 5.6×10^6 L mol^{-1} s^{-1} at 20 °C (Jolley and Carpenter, 1983).

At pH > 5.5, dichloramine formation is significantly slower than that of monochloramine. The reaction rate constant for the formation of dichloramine is 5.27×10^2 L mol^{-1} s^{-1} at 20 °C (Jolley and Carpenter, 1983). The relatively slow formation kinetics of dichloramine explains why it is usually found at much lower concentrations than monochloramine.

A condition often observed in water treatment when chlorine is added to water containing ammonia is the breakpoint phenomenon. As chlorine is added to water in the pH range of 6 to 9, at chlorine to ammonia molar ratios < 1, monochloramine is formed. The combined chlorine residual increases to a peak value. As the chlorine-ammonia ratio is further increased, dichloramine is formed according to Equation 2.5. As dichloramine is unstable under these conditions, it decomposes according to Equation 2.9.

$$2NHCl_2 + H_20 \longrightarrow N_2 + HOCl + 3H^- + 3Cl^- \qquad (2.9)$$

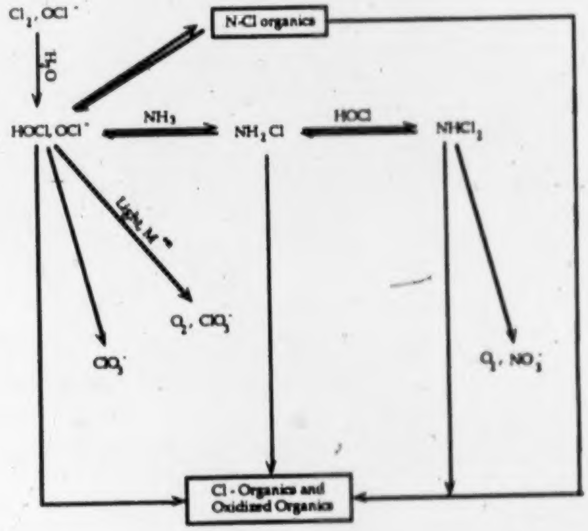
As the ratio of chlorine to ammonia increases from about 1 to 1.65, the measured chlorine residual decreases. Once the breakpoint, where all the ammonia has been oxidized to molecular nitrogen and small amounts of nitrate is reached, introduction of additional chlorine will result in an increase in the total chlorine residual, with chlorine added beyond the breakpoint existing as the free chlorine species HOCl and OCl^-. After the breakpoint, the total chlorine residual will consist of free chlorine plus any combined chlorine present in the form of organic chloramines that were not destroyed by the free chlorine.

Free and combined chlorine species may react through numerous pathways with other compounds present in the water matrix. Free chlorine can react with nitrogen containing organic compounds to form organic chloramines. Although organic nitrogen concentrations may exceed those of ammonia-nitrogen in many waters, present knowledge about the interactions between chlorine and organic amines is very limited. The relative ratio of chloramines and organic-chloramines formed is dependent upon the concentration ratio of ammonia to organic N and on the reaction kinetics. However, there appears to be a transfer of chlorine from monochloramine to organic nitrogen species with time (Jolley and Carpenter, 1983).

Several inorganic compounds other than ammonia readily react with available chlorine. Iron (II), Manganese (II), nitrite, sulfide, sulfate and cyanides rapidly reduce chlorine to chloride, and can exert a significant chlorine demand (White, 1986; Jolley and Carpenter, 1983). These compounds have been identified as interferences in chlorine residual measurements (APHA-AWWA-WPCF, 1989).

Numerous reactions between free chlorine and the complex matrix of organic compounds found in natural waters are possible. The types and concentrations of organochlorine compounds formed are a function of the reactant concentrations, reaction kinetics, equilibria, temperature, pH, and the presence of impurities (Jolley and Carpenter, 1983). Oxidation, addition, and substitution reactions between free chlorine and organic components may occur. Figure 2.1 shows some of the possible reaction pathways for free chlorine in natural waters.

Figure 2.1. Possible reaction pathways for chlorine in natural waters (Adapted from Jolley and Carpenter, 1983).



Several authors have suggested that oxidation may be the predominant reaction occurring between free chlorine and organics found in natural waters (Jolley and Carpenter, 1983;

Jolley et al., 1975). Carbohydrates and similar compounds are examples of organic compounds which undergo oxidation in the presence of free chlorine. Addition reactions occur between hypochlorous acid and organics containing reactive double bonds to form chlorohydrins. In the presence of organic and nitrogen containing organic compounds, chlorine may substitute with hydrogen atoms producing both chlorinated organic compounds and organic chloramines.

An important class of compounds that may be formed through substitution reactions are the trihalomethanes (THMs). THM formation has been found to be dependent on chlorine dose, the organic content of the water, the contact time, and the temperature. The precursors and formation of these volatile compounds have been extensively studied (Stevens et al., 1975). Humic materials have been identified as important THM precursors (Meier et al., 1986). Non-volatile chloro-organics may also be formed by chlorination of humic materials.

Although monochloramine is commonly found in chlorinated waters, little information is available on the reactions of chloramines with the inorganic and organic constituents of freshwaters. Chloramines are less reactive oxidants than free chlorine species, and may therefore be the predominant species in receiving water systems. Although interactions between chloramines and organic materials have not been as extensively studied as similar reactions with free chlorine, monochloramine is known to participate in several reactions of environmental significance.

Jolley and Carpenter (1983) suggested that the principal reactions of monochloramine result from hydrolysis to hypochlorous acid and from active chlorine transfer. They further theorized that similar products should be formed as those arising in reactions between free chlorine and other organic and inorganic constituents due to the continuous hydrolysis of monochloramine to hypochlorous acid. However, these products would be expected to be present at lower concentrations due to the lower equilibrium concentrations of HOCl. Monochloramine is an active agent in the transfer of chlorine to the amino substituent of primary and secondary aliphatic amines, peptides, and amino acids, and is also known to undergo electrophilic aromatic substitution reactions (Pierce, 1978).

Trihalomethane formation in the presence of monochloramine is reduced from that seen with free chlorine. However, the formation of higher quantities of non-purgeable organic halogens from chloramines over that observed with free chlorine indicates that chloramines may be more likely to form chlorinated organics through substitution reactions (Jensen et al., 1984).

2.1.2 Chlorine Fate and Decay in Natural Waters

To date, most research investigating the decay of chlorine residuals has involved laboratory studies in distilled water. Direct application of these results to the consideration of chlorine decay in the receiving environment may not be valid due to the difficulty of adequately modelling the dominant in-stream physical and chemical processes governing decay in the laboratory. Prior research on chlorine decay in the receiving environment has concentrated on discharges of cooling water effluents from fossil-fuel generating stations and chlorinated sewage treatment effluents. No literature investigating the environmental behaviour of residual chlorine specific to water treatment plant effluents was found. Consequently, information relevant to this study was extracted from studies of chlorine decay in other effluents. General application of the results from these studies should be valid. However, differences in chlorine speciation and demand will exist due to significant variations in the chemical composition of the discharge and receiving waters specific to each effluent.

The processes by which residual chlorine is removed from aqueous solution are not well understood, and current knowledge of the various processes is at a very rudimentary level. Several mechanisms for the decay of residual chlorine in natural aquatic systems have been identified. Høstgaard-Jensen (1977) suggested the following mechanisms were responsible for the removal of residual chlorine from cooling waters: volatilization to the atmosphere; reactions with inorganic compounds causing reduction of chlorine to chloride; reaction with organic material to form chloride by addition to a double bond, substitution reactions to form an organo-chlorine compound, and oxidation to a higher oxidation level or to CO_2 and water; and UV catalyzed decomposition of free chlorine. Furthermore, adsorption to sediments, adsorption and reactions with benthic materials, and interactions with biological constituents may also result in the depletion of chlorine residuals. The ultimate decomposition products of residual chlorine in natural freshwaters are chloride, oxidized organics, chloroorganics, oxygen, nitrogen, chlorate and nitrate (Jolley and Carpenter, 1983).

Chlorine decay kinetics in natural waters are most often described by a first-order process following Equation 2.10 (Lin et al., 1983; Gowda, 1981; Jolley and Carpenter, 1983; Qualls and Johnson, 1985; Reckhow , 1990; Abdel-Gawad and Bewtra, 1988).

$$C = C_0 e^{-kt} \tag{2.10}$$

However, several recent investigators have suggested that a second-order equation more accurately describes their experimental data (Leao and Selleck, 1983; Yamamoto et al., 1988). Although there is some dispute over the proper form for the rate expression, it appears that the majority of researchers have found that chlorine decay is most accurately described using a first-order model.

Several investigations under both laboratory and field conditions have attempted to quantify the rate of decay of chlorine residuals. A summary of reported decay rates for residual chlorine species under a variety of environmental conditions can be found in Table 2.1. The reported rate constants vary widely, over several orders of magnitude. This wide range may result from the variation in water qualities tested, and to the difficulties of adequately simulating the complex array of processes occurring in the receiving stream. As a generalization, the U.S. EPA (1984) has stated that field decay rates are approximately an order-of-magnitude greater than those observed in the laboratory.

2.1.2.1 Chemical Decomposition

In the presence of ammonia compounds, free chlorine in natural waters combines quickly to form chloramines, and an understanding of the decay mechanisms of chloramines is necessary. In natural systems, chlorine is usually assumed to exist predominantly as monochloramine and small quantities of other combined chlorine species, with a negligible free chlorine residual (Reckhow, 1990; Yamamoto et al., 1988; Lin et al, 1983; Brungs, 1973). This is probably a valid assumption where an adequate supply of ammonia nitrogen is present, as the reaction between free chlorine species and ammonia is very rapid ($k=10^{10}$ L mol^{-1} h^{-1}) (Leao and Selleck, 1983). Dichloramine and trichloramine (nitrogen trichloride) are only found at significant concentrations in waters with high applied chlorine to nitrogen ratios (> 5:1) or low pH (Yamamoto et al., 1988). Due to its relative stability, monochloramine is the major species of residual chlorine of concern when assessing the environmental impacts of chlorine discharges into the receiving environment (Reckhow, 1990; Yamamoto et al., 1988).

Leao and Selleck (1983) proposed a series of reactions to describe the transformations and decay of combined chlorine residuals over time in waters with excess ammonia. This model incorporated redox pathways that had been previously used to describe reactions occurring when excess free chlorine was present. Although it has been suggested that

Table 2.1 Literature survey of reported first-order chlorine decay rates

Chlorine Species	pH*	Temp* (°C)	k (d^{-1}) (base e)	Water Matrix †	Comments	Literature Source
monochloramine	7.4	18	0.11	river	batch test in dark	Lin et al., 1983
monochloramine	7.4	20	1.84	river	batch test in sunlight	Lin et al., 1983
chloramines	n/s	25	18.72	DI	phosphate buffered	Evans, 1982
monochloramine	7.4	18	0.905	river	batch test in sunlight	Lin et al., 1983
monochloramine	n/s	25	1.68	DI	$NH_2Cl + H_2O \leftrightarrow NH_3 + HOCl$	Gray et al., 1979
dichloramine	25	n/s	0.048	DI	$NHCl_2 + H_2O \leftrightarrow NH_2Cl + HOCl$	Gray et al., 1979
monochloramine	n/s	25	0.0653	DI	in phosphate buffer solution	Evans, 1982
chloramines	n/s	25	18.84	DI	in phosphate buffer solution,	Evans, 1982
Free chlorine	n/s	n/s	50.4 to 178	secondary effluent	nitrified secondary effluent exposed to sun / wind	Jolley and Carpenter, 1983
Free chlorine	n/s	n/s	4.6 to 18.5	secondary effluent	secondary effluent with no mixing or UV light	Jolley and Carpenter, 1983
monochloramine	neutral	n/s	0.72 to 1.8	secondary effluent	lab tests	Jolley and Carpenter, 1983
monochloramine	neutral	n/s	6.7 to 7.4	secondary effluent	outdoors experiment	Jolley and Carpenter, 1983
TRC	n/s	n/s	36.9 to 125	river	summer field tests on the Boyne River, Ont.	Gowda, 1978
TRC	n/s	n/s	17.2 to 39.8	river	summer field tests on Aurora Creek, Ont.	Gowda, 1978

* not specified

† Distilled water

Table 2.1 ...continued

Chlorine Species	pH*	Temp* (°C)	k (d^{-1}) (base e)	Water Matrix †	Comments	Literature Source
TRC	n/s	n/s	3.2 to 9.6	river	winter field tests on Aurora Creek, Ont.	Gowda, 1978
free chlorine	4	23	0.019	DI	closed batch test	Suidan et al., 1977
free chlorine	4	35	0.043	DI	closed batch test	Suidan et al., 1977
free chlorine	7.6	23	0.019	DI	closed batch test	Suidan et al., 1977
free chlorine	7.6	2	0.019	DI	closed batch test	Suidan et al., 1977
free chlorine	10	23	0.019	DI	closed batch test	Suidan et al., 1977
free chlorine	10	35	0.019	DI	closed batch test	Suidan et al., 1977
free chlorine	n/s	n/s	11.3 to 23.	potable	in filters, sedimentation tanks at WTP	White, 1986
chloramines	n/s	n/s	< 2.5	potable	in filters, sedimentation tanks at WTP	White, 1986
free chlorine	n/s	n/s	1.7	river	Delaware River water, with photolysis	Dotson and Helz, 1985
free chlorine	n/s	n/s	0.43	river	Delaware River water, with no photolysis	Dotson and Helz, 1985
TRC	n/s	n/s	20 to 30	river	suggested typical values	Cumbie et al., 1985
FRC	8.3	n/s	50.4 to 178	secondary effluent	nitrified secondary effluent exposed to wind/sun	Johnson, 1975
FRC	8.3	n/s	4.6 to 18.5	secondary effluent	nitrified secondary effluent, no wind/sun	Johnson, 1975

* not specified

† Distilled water

Table 2.1 …continued

Chlorine Species	pH*	Temp* (°C)	k (d^{-1}) (base e)	Water Matrix †	Comments	Literature Source
monochloramine	8.3	n/s	6.7 to 7.4	secondary effluent	nitrified secondary effluent exposed to wind/sun	Johnson, 1975
monochloramine	8.3	n/s	0.72 to 1.8	secondary effluent	nitrified secondary effluent, no wind / sun	Johnson, 1975
TRC	n/s	20	0.65	secondary effluent	quiescent, open to atm., 12h light/dark exposure	Abdel-Gawad and Bewtra, 1988
TRC	n/s	20	1.32	secondary effluent	quiescent, open to atm., 12h light/dark exposure	Abdel-Gawad and Bewtra, 1988
TRC	n/s	20	0.65	secondary effluent	turbulent conditions, open to atm., in dark	Abdel-Gawad and Bewtra, 1988
TRC	n/s	20	0.08	secondary effluent	estimated for photolytic degradation	Abdel-Gawad and Bewtra, 1988
Free chlorine	n/s	14	1.58	groundwater	batch test in flasks	Wable et al., 1990
Free chlorine	n/s	14	2.88	potable	Seine treated water (Ivry),	Wable et al., 1990
Free chlorine	n/s	14	1.15	potable	Seine treated water (Orly),	Wable et al., 1990
TRC	n/s	n/s	7.6	sewage	unaerated sample	Singleton, 1989
TRC	n/s	n/s	0.37	sewage	primary effluent	Singleton, 1989
TRC	n/s	n/s	0.25	sewage	aerated lagoon effluent	Singleton, 1989
TRC	n/s	n/s	13.3 to 40	river	Maumee River, Ohio	Plumb et al., 1979
TRC	n/s	n/s	0.4 to 4.0	lake	cooling water discharges	Lawler et al., 1985

* not specified

† Distilled water

Table 2.1 ...continued

Chlorine Species	pH*	Temp* (°C)	k (d^{-1}) (base e)	Water Matrix †	Comments	Literature Source
TRC	n/s	10	0.58	river	photolytic decay rate in Arkansas River water	Lee et al., 1982
TRC	n/s	10	2.74	river	volatilization rate from Arkansas River water	Lee et al., 1982
TRC	n/s	10	1.73	river	water column demand in Arkansas River water	Lee et al., 1982
TRC	7	25	4.84	DI	3:1 ratio of Cl:glycylglycine (as org-N surrogate)	Qualls and Johnson, 1985
TRC	n/s	20	4.8 to 630	stream	decay rates in natural streams	Gowda, 1981
TRC	n/s	20	1.2 to 23.8	river	water column demand in several Colorado rivers	Heinemann et al., 1981
TRC	n/s	20	0.6 to 21.2	river	photolytic decay rate in several Colorado rivers	Heinemann et al., 1981
TRC	n/s	20	2.7 to 56.0	river	volatilization rate from several Colorado rivers	Heinemann et al., 1981
TRC	n/s	n/s	144	stream	field tests in Lampson Brook, Massachusetts	Reckhow et al., 1990

* not specified

† Distilled water

some of the redox pathways that occur in the presence of free chlorine may not describe the actual reactions that occur when ammonia nitrogen is present in excess, it appears that their application in this model may remain valid as the reactions occur under a similar path (Hand and Margerum, 1983). The dominating reaction or reactions were found to be a function of several system-specific parameters such as temperature, pH, and chlorine dose.

Using the above model, Leao and Selleck (1983) were able to obtain quite accurate predictions of residual chlorine species concentrations with time. They found that at low chlorine to ammonia nitrogen ratios, the disappearance of monochloramine was accurately described by a second order reaction. Dichloramine appeared to be the rate limiting reaction. The above model is only suitable for application in laboratory-grade water, and determination of chloramine decomposition pathways within natural waters is complicated by the numerous competing reactions. A model similar to that developed by Leao and Selleck (1983) that is applicable for use in natural waters has not yet been developed.

2.1.2.2 Water Column Chlorine Demand

The presence of oxidizable organic and inorganic matter within most natural waters creates a demand for residual chlorine within the water column through reactions with these materials. Numerous reactions occur within the water column, over a wide range of time scales (Dotson and Helz, 1985). Oxidation of selective organic sulfur and aromatic and nitrogen heterocyclic rings can occur in less than one second. Over a time frame of seconds to hours, oxidation of organic and inorganic amines accounts for much of the chlorine consumed. Less favourable, and relatively inselective oxidation reactions between more stable organic compounds occur over a time scale of minutes to days.

Considerable effort has been expended to better the current knowledge regarding the reactions between residual chlorine and the other chemical species present within the water matrix. Many studies have investigated the decay kinetics of TRC when exposed to surrogate compounds representing humic and organic matter (Valentine et al., 1988; Jafvert and Valentine, 1987; Qualls and Johnson, 1984; Leao and Selleck, 1983). However, due to the wide variability of water compositions, and the analytical difficulties associated with such studies, a suitable model for predicting TRC consumption rates within natural waters has not yet been developed.

Due to the difficulties in developing a kinetic model for prediction of TRC consumption an natural water, rates of TRC decay are commonly determined through laboratory studies.

Often, water obtained from the receiving stream is injected with a volume of chlorine, and the change in residual with time is monitored. These studies are often conducted in completely closed-systems, where the effects of photolytic degradation and volatilization are minimized. The time-dependent decay of TRC is usually observed to follow first order kinetics, with rate coefficients usually ranging from 0.1 to 30 d^{-1} (Table 2.1).

As this is the easiest mechanism to quantify, water column decay rates obtained in the laboratory are often directly applied to describe rates of chlorine decay within the receiving stream. Application of the results in this manner does not account for the other in-stream processes affecting chlorine decay, and may result in a under-estimation of the actual rate of chlorine loss. Lee et al. (1982) reported a rate coefficient for water column chlorine demand of 1.73 d^{-1}. This value represented approximately 35% of the gross chlorine decay. Heinemman et al. (1981) reported a series of water column demand coefficients, which typically accounted for 9 to 55% of the overall decay rate. Similar results were observed by Abdel-Gawad and Bewtra (1988).

2.1.2.3 Adsorption to Sediments

In rivers with a high sediment loading, it would be reasonable to expect that a portion of the residual chlorine would be adsorbed onto sediment particles. Adsorption is known to be effective in the removal of residual chlorine as adsorptive processes are used for water dechlorination (Montgomery, 1985). Factors that could be expected to affect the degree of adsorption would include temperature, pH, the amount and type of sediment present, particle size distribution, and possible competitive adsorption effects (Weber, 1972). Kinetic effects would also be important, as chlorine residuals would not be expected to persist for a period greater than a few days. A survey of pertinent literature indicates that very little work has been done in assessing the adsorptive capacity of suspended sediments in natural streams for residual chlorine. However, some relevant information may be extracted from available literature describing the adsorptive behaviour of chlorine on granular activated carbon (GAC). The adsorptive behaviour and mechanisms may be similar, yet reaction kinetics and capacities between residual chlorine and aquatic sediments would be expected to be much slower than those observed with GAC.

McCreary and Snoeyink (1981) concluded from a study of the reactions between free chlorine and GAC that, based upon a mass balance of TOX, chlorine reacted with the GAC itself, rather than with sorbed organics or organics in solution. This may be indicative that adsorption of free chlorine onto sediment surfaces may be an important pathway for removal of the residual from the water column.

The reaction kinetics between hypochlorous acid and GAC proceed more quickly than between OCl^- and GAC (Suidan et al., 1977).. Because of the strong dependence of free chlorine speciation upon solution pH, the pH will play a very important role in determining the extent to which adsorptive processes are significant. Suidan et al. (1977) found that decreasing the solution pH of 20 mg/L GAC in 35 °C deionized water from pH 10 to pH 4 resulted in a decrease in time from approximately 235 hrs to 40 hrs to achieve an equivalent removal of residual chlorine from approximately 40 mg/L to 5 mg/L. In the same series of experiments, Suidan et al. (1977) found that temperature, through its effects on the reaction rates, is also significant in determining the degree of adsorption achieved. After a reaction time of 200 hrs, a chlorine solution at initially 40 mg/L was reduced in concentration by 86% at 35 °C, while at 2 °C, an equivalent solution was reduced by only 55 %.

The presence of organic compounds may also influence the rate and degree of uptake of free chlorine by the adsorbate. Reactions between sorbed species and residual chlorine may increase the observed uptake rates. However, competitive adsorption for the limited adsorption sites may also result in a retardation of chlorine adsorption due to displacement of the sorbed chlorine by more readily adsorbed organic compounds. Based on theoretical principles, adsorption of TRC onto sediments is possible. However, considerable research is required to determine if the adsorption kinetics and capacity of the sediments are sufficient to make this a significant sink within the natural system.

2.1.2.4 Benthic Demand

A certain capacity for the uptake of residual chlorine may exist within the benthic layer of natural streams. Riverbeds below wastewater outfalls may be covered with highly active biological materials, biological slimes, sludges, and algae (Krenkel and Novotny, 1980). The growth and accumulation of these deposits can result from deposition of suspended organics and the transfer of soluble organics from the flowing waters into the bottom sediments. The rate of uptake of a pollutant by the benthic layer is a function of many variables including: temperature, pollutant characteristics, flow regime, depth, sediment characteristics, the presence of slime and bottom deposits, benthal organism population and speciation, and the organic content of the bottom sediments (Krenkel and Novotny, 1980; Rinaldi et al., 1979).

The relative degree to which these deposits may contribute to the overall chlorine demand of the system will be dependent upon factors similar to those influencing the uptake by suspended sediments. The amount of chlorine that reacts with biological growths within this layer will be very dependent upon the overall water quality, but may be significant in highly polluted streams and downstream of sewage treatment outfalls. The degree of importance that benthic demand exerts for residual chlorine is uncertain, however, this represents a significant sink in dissolved oxygen modelling, and may contribute to the overall chlorine demand within the system.

2.1.2.5 Volatilization

Very little work to date has focussed upon determining the relative importance of volatilization in residual chlorine loss mechanisms for natural streams. Losses due to volatilization will be dependent upon chemical properties of the chlorine species, properties of the stream, and atmospheric conditions. Due to the low molecular weight of the prevalent inorganic chloramines, volatilization may constitute an important removal pathway.

Important chemical properties influencing the volatility would be the solubility and Henry's Law constants of the individual chlorine species. Henry's Law, defined by Equation 2.11, relates the equilibrium partitioning of a compound between the air phase and the liquid phase.

$$C_a = \frac{H}{RT}\ C \qquad (2.11)$$

where: C_a = liquid phase concentration (mg/L)
C = aqueous phase concentration (mg/L)
H = Henry's Law coefficient (atm m^3 mol^{-1})
R = universal gas constant (atm m^3 mol^{-1} K^{-1})
T = temperature (K)

Free chlorine is highly soluble from the basis of this investigation, with a solubility of 7290 mg/L at 20 °C (White, 1986). Reckhow et al. (1990) reported an estimate of the Henry's Law coefficient for TRC of 0.0055 ± 0.0006 atm m^3 mol^{-1}: monochloramine was reported as the dominant species. A Henry's Law coefficient of 0.014 atm m^3 mol^{-1} for molecular chlorine has been reported by the American Water Works Association (1990). Few reported Henry's Law constants are available for aqueous chlorine species, perhaps due to the instability of these compounds. Molecular chlorine (Cl_2) would be expected to be the most volatile TRC species, with hypochlorous acid, monochloramine, dichloramine and trichloramine following in order of decreasing volatility. While the Henry's Law coefficient describes the equilibrium partitioning of a compound between the aqueous and gaseous phases, it does not state the rate at which, if ever, this equilibrium is achieved.

Stream properties such as the degree of turbulence and the channel aspect ratio are also important factors affecting volatilization losses, primarily through their effects on the transfer rates. In highly turbulent streams, a consistent chlorine concentration would be maintained throughout the water column, and a constant concentration of chlorine would be maintained at the water-air interface. In such cases, the rate of volatilization will be limited by transfer to the gas phase, and the equilibrium concentrations will be governed by Henry's Law. In less turbulent and in deeper streams, there may be somewhat less interaction with the surface layer, resulting in lower rates and amounts of volatilization. Several environmental factors which may reduce chlorine transfer efficiency were identified by Reckhow et al. (1990). These included for air-phase limiting transfer: low Henry's Law coefficients, low wind speeds, and high stream turbulence. Liquid phase-limiting steps were identified as high H, high wind speeds, and lower turbulence.

In a study of chlorine distribution downstream of a municipal wastewater outfall, Reckhow et al. (1990) concluded that volatilization was the dominant loss mechanism. Commonly, compounds with a Henry's Law coefficient greater than 0.001 are assumed to be highly volatile, with the transfer mechanism being liquid-phase limited (Lyman et al., 1982). However, Reckhow et al. (1990) found that air samples collected immediately above the stream were "saturated with respect to the liquid-phase CRC concentration", leading to the conclusion that chlorine transfer was air-phase limited. The authors recognized that this conclusion represented an exception to accepted mass-transfer theory.

While the conclusions of Reckhow et al. (1990) must still be considered preliminary, they are similar to those reported by others. Using an analytical method as reported by Tsivoglou (1967), and comparing the rate-constants obtained to water column demand and photolytic demand rate-constants determined in the laboratory, Heinemann et al. (1981) found that volatilization accounted for over half of the lost chlorine in several Colorado Front Range rivers, with chemical reactions and photolysis accounting for the remaining decay. Abdel-Gawad and Bewtra (1988) found that the chlorine decay rate coefficient doubled with the application of turbulence in bench-scale chlorine-decay tests. They attributed this increase to a more rapid-renewal of the liquid and air films which permitted increased volatilization rates.

2.1.2.6 Photolysis

Photolytic decomposition of residual chlorine has been reported as a significant process in laboratory systems exposed to UV light. Several investigators have reported an increase in the chlorine decay coefficient of an order of magnitude between samples exposed to ultraviolet light and those maintained in the dark (Lin et al., 1983; Jolley and Carpenter, 1983; White, 1986; Johnson, 1975) (See Table 2.1). The rate of photolytic decomposition varies between chlorine species. Photolytic decomposition is most pronounced for free chlorine, while the chloramine species are considerably more stable under UV light. It is usually modelled as a first-order process.

Application of laboratory results to field situations appears to yield contradictory results. While many laboratory studies have reported UV light to greatly increase the rates of chlorine decay, the limited field data available have not confirmed this. Conversely, most field investigators have arrived at the conclusion that UV decay is an insignificant contribution to the gross rate of chlorine decay. Abdel-Gawad and Bewtra (1988) found that photolytic decomposition accounted for approximately 10% of the observed decay rate between samples exposed to no light and those exposed to alternating periods of light and dark. They reported photolytic rate constants (k_p) of 0.03 d^{-1}. In a series of light and dark bottle tests, Reckhow et al. (1990) found that photolysis decay constants were approximately an order of magnitude less than the rate constants for chemical demand, reporting k_p values of 0.72 to 2.64 d^{-1}. Similarly, Heinemann et al. (1981) reported phototransformation rate constants obtained from light-bottle dark-bottle tests ranging from 0.58 to 14.4 d^{-1}. These typically represented 5 to 30% of the overall decay rate.

The apparent difference between laboratory and field date may possibly be explained by consideration of the physical behaviour of the systems and the speciation of TRC present. Most laboratory tests are performed under controlled conditions, and processes such as volatilization may be minimized. In these cases, the relative magnitude of k_p in relation to the other processes may increase substantially, and it may indeed become the dominant decay mechanism. As well, while many of the laboratory studies have been performed using free chlorine, TRC within the environment exists primarily as monochloramine; a much more stable compound under UV light.

Rates of phototransformation increase with increasing pH due to an increased quantum yield. This may be an important consideration in rivers that experience pH variations due to algal growth or other causes Heinemann et al. (1981). Stream turbulence is another factor which would be expected to influence the extent of photolytic decay. In very turbid streams, UV penetration would be greatly retarded, resulting in reduced photodecomposition.

2.1.2.7 Temperature effects

Chemical decay of chlorine is a temperature dependent process, with the rate being retarded at reduced temperatures. The affect of temperature on the rate of chlorine decay is usually described by a modified van't Hoff-Arrhenius equation as described by Gowda and Post (1984),

$$k_{T_2} = k_{T_1} \, \theta^{(T_2 - T_1)} \qquad (2.12)$$

where k_{T_1} and k_{T_2} represent the decay rate coefficients at temperature (°C) at T_1 and T_2 respectively, and θ is the temperature correction factor.

Using values for the activation energy of monochloramine, as reported by Fair and Geyer (1961), Gowda (1978) reported values of θ for a temperature range of 4 °C to 25 °C and a pH range of 7.0 to 8.5 of 1.025 to 1.031. For practical purposes, $\theta = 1.03$ was recommended. Abdel-Gawad and Bewtra (1988) reported a temperature correction factor, θ, of 1.08 based on a series of laboratory tests conducted over a temperature range of 2 to 30 °C.

Theoretically, most parameters used to describe ecological processes are temperature dependent due to the strong dependence of reaction rates on temperature. Quantification of this temperature dependence may be very important for certain applications. However, in river and fate modeling, the temperature dependencies are small, and they may often be justifiably neglected when compared with the uncertainties inherent within the model structure (Rinaldi et al., 1979).

2.2 River Mixing

2.2.1 Transverse Mixing Theory

Following discharge into a stream, a soluble, neutrally bouyant pollutant is diluted through the combined effects of several hydraulic transport processes. Advection, convection, and molecular and turbulent diffusion may all contribute to the dispersion of a pollutant within a natural body. Within a flowing stream, advection and turbulent diffusion are the primary processes governing the rate of dispersion.

Molecular diffusion is the movement of a solute within a stream by random molecular motions. It is driven by concentration gradients of the pollutant which exist within the stream. The pollutant moves from areas of high concentration to areas of lower concentration, and the movement may be described by Fick's Law and the classical diffusion equation (Fisher et al., 1979). Turbulent diffusion is somewhat analogous to molecular diffusion, but the driving force for particle scattering is the turbulent motion of the stream. Turbulent diffusion coefficients in flowing streams can be several orders of magnitude larger than the molecular diffusion coefficients. Consequently, turbulent diffusion is the predominant diffusion mechanism in most river systems.

Mixing due to differential advection is an important mixing mechanism in river flows, where significant shear flows and velocity gradients exist. Both vertical and transverse velocity gradients are found in rivers. These velocity gradients will tend to disperse an effluent in the vertical, transverse, and longitudinal directions.

The mixing of a substance in a river can be described by the three-dimensional mass transport equation (Elhadi et al., 1984; Fisher et al, 1979)

$$\frac{\partial C}{\partial t} + U\frac{\partial C}{\partial x} + V\frac{\partial C}{\partial y} + W\frac{\partial C}{\partial z} = \frac{\partial}{\partial x}\left(\varepsilon_x\frac{\partial C}{\partial x}\right) + \frac{\partial}{\partial y}\left(\varepsilon_y\frac{\partial C}{\partial y}\right) + \frac{\partial}{\partial z}\left(\varepsilon_z\frac{\partial C}{\partial z}\right) \quad (2.13)$$

where C is the pollutant concentration, U, V, and W are the longitudinal (x), vertical (y) and transverse (z) velocity components, and ε_x, ε_y, and ε_z are the corresponding turbulent diffusion coefficients. A summary of the rational and assumptions used to reduce Equation 2.13 to a form amenable to a numerical solution of the transverse mixing problem is described below. Detailed discussion of the derivation of this equation can be found elsewhere (Somlyódy, 1981; Holley et al., 1971; Beltaos, 1979; Elhadi et al., 1984)

Due to the shallow depth and highly turbulent motion of most streams, vertical mixing within a river is accomplished relatively quickly. A common approximation is that no significant vertical concentration gradients exist beyond a very short distance downstream from the discharge point. Elhadi et al. (1984) suggested that the approximate distance required for complete vertical mixing could be calculated as

$$\frac{x_v}{h} = 1.8\,\frac{U}{u_*} \tag{2.14}$$

where: x_v = distance required for vertical mixing
h = depth
U = mean velocity in the longitudinal direction
u_* = shear velocity.

They suggested that the distance required for essentially complete vertical mixing was on the order of 30 channel depths. Other researchers have similarly suggested that complete vertical mixing in a river will occur in less than 100 depths (Fisher et al, 1979; Beltaos, 1978).

It is apparent that, in situations where the flow field depth is small in comparison with its width, the pollutant concentration distribution quickly becomes uniform with depth. However, a considerable distance remains over which significant transverse concentration gradients are present. In this region, the mixing can be considered two-dimensional, with variations only in the longitudinal and transverse directions. This region is termed the transverse mixing zone. Beyond this point, mixing occurs only within the longitudinal direction. The length of the transverse mixing zone can be very long, and as it scales on the square of the channel width, complete transverse mixing may never occur in very wide rivers (McCutcheon, 1989; Fisher et al, 1979). Similarly to Equation 2.14, Elhadi et al (1984) proposed an order-of-magnitude approximation to determine the longitudinal distance required to achieve complete transverse mixing.

$$x_m = \frac{0.5\,U\,\left(\frac{B}{2}\right)^2}{E_z} \tag{2.15}$$

where: x_m = distance required for transverse mixing
U = mean velocity in the longitudinal (x) direction
B = channel width
E_z = transverse mixing coefficient.

Using the same example as for vertical mixing, they found that the effluent would require a downstream distance exceeding 600 channel widths to achieve a completely mixed state.

Assuming a steady-state discharge, depth-averaging, and assuming that the term representing dispersive transport in the longitudinal direction is small compared to the advection term, Equation 2.13 can be simplified to Equation 2.16. The transverse growth of a conservative, neutrally bouyant pollutant which is completely mixed in the vertical can therefore be described by (Beltaos, 1979):

$$h\frac{\partial c}{\partial t} + hu\frac{\partial c}{\partial x} = \frac{\partial}{\partial z}\left(hE_z\frac{\partial c}{\partial z}\right) \qquad (2.16)$$

Equation 2.15 is applicable only to prismatic channels. The dispersion coefficients in Equation 2.13 have been replaced by the transverse mixing coefficient E_z. The transverse mixing coefficient incorporates the combined effects of diffusion, differential advection, and the effects of secondary currents.

To account for the effects of local variations in stream geometry, velocity, and secondary currents which exist in natural channels, Yotsukura and Cobb (1972) introduced the concept of a dimensionless transverse coordinate system defined as

$$q(z) = \int_{o}^{z} uhdz \qquad (2.17)$$

where q represents the cumulative streamflow, z = 0 represents the left bank (looking downstream) and h and u respectively denote the depth and local depth-averaged velocity. At the right bank, z = W, the total stream width, and q = Q, the total discharge.

Introducing the above streamtube transformation into Equation 2.16, assuming steady-state conditions, and with concentration (c') and transverse location (η) expressed in dimensionless forms, the two-dimensional, depth-averaged mixing equation reduces to

$$\frac{\partial c'}{\partial x} = \frac{1}{Q^2}\frac{\partial}{\partial \eta}\left(uh^2E_z\frac{\partial c'}{\partial \eta}\right) \qquad (2.18)$$

where $\eta = \frac{q}{Q}$ and $c' = \frac{c}{c_\infty}$, where c_∞ = the completely-mixed pollutant concentration.

Equation 2.18 can be modified to account for the non-conservative behaviour of a pollutant such as chlorine by inclusion of a first-order decay term as per Equation 2.10.

$$\frac{\partial c'}{\partial x} = \frac{1}{Q^2} (uh^2 E_z \frac{\partial c'}{\partial \eta}) - \frac{kc'}{u} \qquad (2.19)$$

Equation 2.18, which represents the steady-state, depth-averaged, two-dimensional advection - diffusion equation in dimensionless form is applicable to use in natural channels. In this form, the equation is amenable to a numerical solution, and several models have been developed.

2.2.2 The Transverse Mixing Coefficient

Given information on the channel geometry and discharge characteristics, a numerical solution of Equation 2.19 is possible. Often, the major unknown required for the solution is the transverse mixing coefficient E_z. The solution is highly dependent upon the value of E_z choosen, yet it is a highly variable parameter and little guidance in the selection of E_z is available. Much effort has been expended to allow prediction of the transverse mixing coefficient based on channel data; however, no reliable theoretical method has yet been developed.

Several laboratory studies to determine E_z have been performed, with the results summarized by Lau and Krishnappen (1977) and Beltaos (1978, 1979). These studies have shown E_z to be dependent on the friction factor and the channel aspect ratio, but the results are variable and not directly applicable to the variable geometry of natural streams. Studies of the transverse mixing coefficient in natural streams have indicated that it is generally larger than would be suggested based on laboratory results, resulting from increased transverse dispersion due to differential advection. Lau and Krishnappen (1981) suggested that E_z may also be dependent on the channel sinuosity, the ratio between the thalweg length and the down valley distance. The sinuosity provides a characterization of the stream curvature over an extended section of the river.

The results of available field tests have been summarized by Beltaos (1979) and Elhadi et al. (1984). Although many studies have attempted to determine a relationship between the transverse mixing coefficient and stream geometry, no sufficient theory has yet been found. Currently, no valid analytical method is available for selecting values of E_z, and field studies are required to obtain a site-specific estimate.

The transverse mixing coefficient is defined as

$$E_z = \beta \, l \, u_* \tag{2.20}$$

where β is a constant dimensionless mixing coefficient, l is a general length scale representing turbulent eddy size, and u_* is the shear velocity. E_z includes both the effects of turbulent transverse diffusion and transverse dispersion due to the presence of any mean secondary currents.

The transverse mixing coefficient is generally considered to be a function of some length scale, and some measurement of turbulent intensity. The length scale represents the size of the turbulent eddies governing the mixing, while the intensity of the turbulence is related to the boundary shear stresses. The shear velocity u_* is often used as a measure of boundary shear stress in natural streams. Although it has been suggested that the use of a local value of u_* may be more appropriate than a section-averaged value, Lau and Krishnappen (1981) found that allowing u_* to vary across the cross section did not improve concentration predictions.

While it is frequently accepted that the shear velocity is a suitable parameter from which to scale the intensity of turbulence, no one length scale is currently in use. Several length scales have been used, including mean channel width, mean channel depth, hydraulic radius, and the half-plume width. Turbulent motion in a wide river is very dependent upon the boundary stress induced by the streambed, and many investigators have considered a vertical scale such as the hydraulic radius or channel depth as the most appropriate. Lau and Krishnappen (1981) suggested that the larger-scale transverse eddies present in all irregular channels may provide the most effective mixing. The authors analyzed all applicable field data in the literature and concluded that the data could best be correlated when the mixing coefficient was scaled on the channel width. They therefore suggested that the stream width be used as an alternative scale. A similar recommendation was made by Smith and Gerard (1981), where they showed that if the transverse mixing coefficients reported in the literature are scaled using stream width instead of depth, the variation may be somewhat larger, but is more systematic and indicative of the geomorphology of the stream.

A series of field investigations conducted on the Slave River at Fort Smith, NWT found that the half-plume width $\bar{b}$ was the best length scale for non-dimensionalizing E_z (Putz, 1983; Gerard et al, 1985). This was based upon analysis of the mixing of a plume along the near-bank zone of a wide river. The half-plume width is defined as the transverse distance from c'_{max} to the point where $c' = 0.5\, c'_{max}$. Gerard et al. (1985) suggested that $\bar{b}$ was a more appropriate measure of the size of the horizontal eddies in the near–bank region of this wide river than the channel width would be.

The transverse mixing coefficient will vary with the longitudinal position in the river. Reach-averaged values are often used, but solution accuracy may be improved by considering the spatial variation of E_z. Lau and Krishnappen (1981) investigated the effect of varying E_z in both longitudinal and transverse directions when modelling the downstream dispersion of an effluent from a bank outfall. They concluded that E_z should be allowed to vary between cross sections, but that allowing E_z to scale on local depth and vary with transverse position across the cross section did not improve their model predictions.

2.3 Effluent Discharge Modelling

2.3.1 Available models

Several numerical models designed to predict the downstream concentration of a neutrally-bouyant, passive pollutant discharged into a river are available (McBride and Rutherford, 1984; Beltaos and Arora, 1983; Chapman, 1982; Gowda, 1980; Harden and Shen, 1979; Krishnappen and Lau, 1985; Luk et al., 1990; Putz et al., 1984; Ruthven, 1971; etc.). They are all based upon sound fluid mechanics theory, and differ only in the numerical solution technique and the level of flexibility which they afford the user.

2.3.2 TRSMIX

TRSMIX, a model developed by Putz et al. (1984) was selected for use in this study. TRSMIX is a numerical mixing model which incorporates the combined effects of mixing and first-order decay to predict the distribution of discharges into streams and is used in this study to model the observed plume mixing and decay behaviour. It has been used to predict downstream pollutant concentrations observed in field studies on the Slave and Mackenzie Rivers in the Northwest Territories, under a variety of open-water and ice-covered conditions. TRSMIX differs from many of the above-mentioned models in that it is able to model non-conservative pollutants through the inclusion of a first-order decay term.

TRSMIX is based upon implicit finite difference approximations of the two-dimensional steady-state advection-diffusion equation. It is very similar to the model RIVMIX, developed by Krishnappen and Lau (1985), but assumes the metric scaling coefficient is equal to unity with the longitudinal axis following the stream thalweg. The discretization and solution procedure used is that developed by Stone and Brian (1963). This procedure uses weighting coefficients in the difference expressions used to approximate the first-order derivatives, and a Crank-Nicholson expression to approximate the second-order derivative. The weighting coefficients of Stone and Brian were selected to minimize numerical dispersion and oscillations. Through use of the streamtube approach developed by Yotsukura and Cobb (1972), it is able to accurately manage the variable hydrography encountered in natural channels. Putz et al. (1984), Putz(1984) and Putz (1983) should be consulted for a more detailed discussion of the theory and operation of TRSMIX.

2.4 Environmental Impacts of Chlorinated Discharges

A search of the literature revealed that similar to chlorination chemistry, little work specific to chlorine discharges from water treatment plants was available. However, concerns of harmful environmental impacts resulting from chlorine discharges from municipal sewage treatment plants has resulted in the compilation of a considerable database of effluent toxicity. Information on discharges from cooling water plants also have provided some insight into the environmental impact associated with the discharge of chlorinated effluents. Several of the observations and results from the above studies will be of relevance to the assessment of chlorinated water treatment plant outfalls.

Three types of environmental hazards can be associated with the discharge of chlorinated effluents. Cumbie et al. (1984) identified these as potentially toxic effects to humans through the ingestion of residual chlorine from downstream drinking water intakes, concern of the toxic effects from the formation of chlorinated organics, and potentially toxic effects of residual chlorine on aquatic biota within the receiving waters. The toxic effects on humans through the consumption of residual chlorine in downstream drinking water sources is minimal, as residual chlorine concentrations within water treatment plant effluents are well below any potentially toxic level. Through the effects of decay and dilution, residual chlorine at any downstream intake would be well below the 10 mg/L level that is safe for human consumption (Cumbie et al., 1984).

The second impact identified, the toxic effects of chlorinated organics, also does not represent a significant hazard. Although this may be a valid concern in chlorinated municipal sewage treatment plant effluents where substantial organic matter is present, modern drinking water treatment practices are designed to minimize the formation of chloro-organics. It would be expected that the levels of chlorinated organics that may be discharged from the treatment plant would be well below any acutely toxic level. Reactions of residual chlorine in the discharge with organics present in the receiving stream may also produce quantities of chlorinated organics. The chlorinated compounds formed from these reactions would probably be primarily halomethanes (Cumbie et al., 1984). These compounds are highly volatile, and would not be expected to persist long within the water column (Mattice, 1976). As well, water treatment plant effluents, which typically discharge approximately 2.0 mg/L total residual chlorine, any trihalomethanes produced would probably be in quantities well below the Canadian drinking water regulations maximum acceptable concentration of 0.35 mg/L (Health and Welfare Canada, 1989).

The greatest concern with the discharge of chlorinated waters is the possible toxic effects which may occur to the aquatic biota in the receiving stream (Environment Canada, 1987). Numerous toxicological studies have been performed to determine organism response to residual chlorine, with toxic effects being observed at very low residual levels. These studies have shown that the impacts of chlorinated discharges have be influenced by many water quality parameters such as pH, organic carbon, ammonia concentrations, temperature, chlorine speciation, and specific organism sensitivities and contact times. Aquatic plants have proved to be less sensitive to residual chlorine than fish and invertebrate species (Environment Canada, 1987).

An extensive amount of literature on residual chlorine toxicity has been compiled, and should be consulted for a more detailed discussion (Beak Consultants Ltd, 1990; Singleton, 1989; U.S. EPA, 1985; Katz, 1977; Turner and Thayer, 1980; Brungs, 1973). Results from these studies are summarized below. Both fish and invertebrate species exhibit similar ranges of sensitivity to chlorine. Acutely toxic chlorine levels were summarized by the U.S. EPA (1985) for 33 species in 28 genera. The mean acutely toxic levels ranged upwards from 0.028 mg/l for the cladoceran *Daphnia Magna*, with this consistently being the most sensitive species tested. Acute toxicity has been observed in rainbow trout and the pugnose shiner at TRC concentrations of 0.04 and 0.045 mg/L. The rate of mortality is generally rapid, with usually half the mortalities in 96 hour tests occurring in the first 12 hours. The dose-response curve is steep, and 100% toxic responses have been observed at concentrations only three times greater than those at which no toxic response was seen.

The toxicity of residual TRC is a function of the species of TRC present. Free chlorine species such as hypochlorous acid and hypochlorite ion exhibit the greatest toxicity, followed by the chloramines (Environment Canada, 1987). However, for regulatory purposes, all TRC species are considered as equally toxic.

2.5 In-stream Chlorine Standards and Guidelines

The Canadian Water Quality Guidelines (Environment Canada, 1987) has established a guideline of 0.002 mg/L as measured by the amperometric titration (or equivalent) method. This value was established for the protection of freshwater aquatic life. Many Canadian provinces have adopted, or propose to adopt this value. Alberta Environment has proposed the Canadian Water Quality Guidelines standard of 0.002 mg/L be adopted for effluents from the City of Edmonton's water treatment plants (Alberta Environment, 1988). Other jurisdictions including the Ministry of Environment's in Ontario and Manitoba and the International Joint Commission have recommended this limit (Environment Canada, 1987).

The Ministry of the Environment of British Columbia has established a recommended criteria for continuous exposure of 0.002 mg/L total residual chlorine (British Columbia Ministry of Environment, 1989; Singleton, 1989) for the protection of freshwater aquatic life. For controlled intermittent discharges, of total duration in any 24 hour period not exceeding 2 hours, Singleton (1989) recommends the standard for average total residual chlorine concentration should be time-related and should not exceed the value (in µg/L) given by:

$$C = 1074\, t^{-0.74} \tag{2.21}$$

where C is the allowable average total residual chlorine concentration (µg/L) and t is the exposure time in minutes. They furthermore stipulate that at no time should the concentration of TRC exceed a maximum of 100 µg/L. Using the above criteria, duration periods of 30, 60, and 90 minutes yield respective TRC concentrations of 87, 52, and 38 µg/L.

The European Inland Fisheries Advisory Commission recommends a maximum concentration, as hypochlorous acid, of 4 µg/L (Environment Canada, 1987). The equivalent concentration of TRC will vary with temperature and pH, but this corresponds to an approximate TRC concentration of 5 µg/L at pH 7. Current U.S. EPA (1985) guidelines state that freshwater aquatic organisms should not be adversely affected if the 4 day and 1 hour average concentrations of TRC do not, on average, exceed 11 µg/L and 19 µg/L more than once every 3 years (U.S. EPA, 1985). In establishing the Canadian guidelines, Environment Canada (1987) noted that the U.S. EPA values exceeded concentrations at which chronic toxicity was observed in two invertebrate species, and that it equalled the value seen to cause chronic toxicity in the fathead minnow. This is the only species of fish for which chronic toxicity data was available, and it is one that is known to be a relatively tolerant species, less sensitive to chlorine than many others in acute toxicity tests.

3.0 Research Objectives

3.1 Problem Overview

The few previous investigations of chlorine persistence in freshwaters have generally focused upon discharges from either wastewater treatment plants, or from generating station cooling waters. While similarities do exist between these and discharges from water treatment plants, several effluent characteristics are specific to discharges from water treatment plants. The dominant chemical and physical processes through which chlorine decays in the natural environment are dependent upon the form of chlorine present, and on the hydraulic behaviour of the receiving body.

The in-stream distribution of pollutants following discharge into a river is highly dependent upon the mixing regime within the river. Assumptions of complete mixing of an effluent immediately after discharge, especially in large rivers such as the North Saskatchewan, is invalid, and may result in underestimation of the possible environmental impact of these discharges. In-field studies of effluent distribution which attempt to determine decay rates by using observed pollutant concentrations, without consideration of the hydraulic behaviour of the plume will result in inaccurate conclusions as to the actual rate of pollutant decay within the environment.

3.2 Specific Objectives

The primary objective of this study was to determine the rate of decay of residual chlorine present in discharges from the City of Edmonton's two water treatment plants within the North Saskatchewan River. The in-stream distribution of chlorine was determined through comprehensive field investigations of the in-stream chlorine distribution resulting from steady-state discharges of chlorinated waters.

Due to the large size of the North Saskatchewan River, it was not possible to assume that the effluent was completely mixed across the river within a very short distance downstream. It was therefore necessary to determine the site-specific mixing regime of the North Saskatchewan River downstream of the Rossdale and E.L. Smith Water Treatment Plants. This was achieved by conducting steady-state dye tracer studies with Rhodamine WT dye, and modeling the resultant tracer distributions with the mixing model TRSMIX.

The final objective of this study was to gain an improved understanding of the dominant processes affecting the decay and removal of residual chlorine within the North Saskatchewan River. This was achieved by conducting several limited investigations into the possible removal pathways, and assessing the relative contribution of each to the overall decay rate. The effects of photolytic degradation was determined by investigation of the in-stream chlorine distribution downstream of the E.L. Smith Water Treatment Plant at night, when no UV light was present. Benthic chlorine demand was determined by a series of in-situ batch reactor tests, and the water column chlorine demand rate was quantified through study of the rate of decay of total residual chlorine in an isolated reaction chamber.

4.0 Methods and Materials

4.1 Field Investigations

4.1.1 Field Surveys

Field work for the Rossdale study commenced in late August, 1990 and continued into late September. Field work for the E.L. Smith study began in late September, and continued into October. Most of the field work was conducted by two persons, with additional manpower used during the tracer and chlorine plume studies.

Sampling, cross section surveys, and most other field work was conducted using a small, open, flat-bottomed aluminum river boat. When required, such as during the chlorine plume studies, an additional aluminum boat was used. These were both powered by 30 Hp outboard motors, equipped with 'jet-legs' to allow movement in very shallow waters.

Cross sections were selected to provide a representative description of the downstream channel geometry and hydraulic characteristics. Generally, six cross sections were established at each plant, over a 4 km distance. This was felt to provide a reasonable definition of the physical characteristics of the river and discharge plumes over the expected range of chlorine persistence and detection. Cross-sectional geometry at each cross section was determined by sonic sounding surveys using a Raytheon echo sounder. Traverses across the cross section were made, with transverse distance measured with a Topofil®. The cross sectional geometry over the width of the channel was determined by scaling of the resulting profiles.

Measurement of stream velocity profiles at each cross section downstream from Rossdale was conducted on September 11, 1990. Local velocities were measured using a Price current meter (U of A meter No. 670824) according to standard procedures (Riggs, 1988). Bed depth was measured at each station, and due to the shallow depths, current velocity was determined at 0.6h.

Temporary geodetic benchmarks were established at each cross section. Survey hubs along the riverbank were used where necessary, with more permanent objects being selected where possible. All benchmarks were subsequently tied back into Alberta Survey Control datum. A summary of all benchmarks used and established is provided in Table 4.1.

Table 4.1 Summary of temporary and permanent benchmarks

Benchmark	Cross-section	Elevation	Description
E.L. Smith Water Treatment Plant			
ASC296723		628.838	E.L. Smith WTP. 8 m E of curb, 7 m S of low lift pump sign on entrance road to low lift pumps
BM10	discharge	626.338	NE corner of top ledge on concrete outfall structure.
TBM 1	1	620.692	Hub @ x-sect. 1. On gravel bar 30.2 m from BM1
BM1	1	624.156	Spike in first tree immediately u/s of Chevron plant clearing.
TBM2	2	620.741	Hub on bank. 5.5 m from BM2
BM2	2	624.609	Spike in tree up bank.
TBM3	3	620.714	Hub on bank. 2.8 m from BM3
BM3	3	624.23	Spike in low tree stump. 10 cm North of tree with flagging.
TBM4	4	620.573	Hub on bank. 3.6 m from BM4
BM4	4	623.653	Spike in tree stump up bank. Approx. 3 m d/s of tree with flagging.
TBM5	5	621.038	Two stakes bound together approx. 5 m up bank. No permanent benchmark.
TBM6	6	619.919	Hub on bank. Approx. 7.6 m from BM6.
BM6	6	621.653	Spike in tree on d/s side of access road. Approx 15 m from Sept. water level.
BM60	6	626.251	NE corner of concrete structure 100 m up access road. 5 m West of green building.
ASC17392		628.416	Terwillegar Park @ green post 100 m W of 2nd power pole S of pole w/ transformer, centre boat launch
Rossdale Water Treatment Plant			
ASC332270		622.455	NE corner of 101 St., 95 Ave.
BM10	1	617.567	Spike in tree along bike path. Approx. 20 m u/s of u/s end of gravel pile along bank.
TBM1.1	1	614.946	Upstream hub on bank.
TBM1.2	1	614.473	Downstream hub on bank. Approx. 10 m d/s of BM1.1. Behind rock.
TBM2.1	2	614.27	Hub on bank, on flats. (not located 16/10/90)
TBM2.2	2	615.283	Hub under tree, higher up bank.
BM20	2	618.508	Spike in tree. First big tree immediately d/s of clearing with benches.
TBM3.1	3	614.999	Hub along bank. 20 m d/s of TBM3.2
TBM3.2	3	614.177	Upstream hub along bank. Just u/s of concrete debris.
BM30	3	620.122	Spike in tree on river side of bike path. Approx. 8 m u/s of sign on bike path.
BM31	3	620.87	South-east (near left when facing) corner of concrete base on sign on bike paths.
BM 32	3	626.814	NW corner of small (1 m) post on SW corner of bike path. Below convention centre @ construction x-ing.
TBM4.1	4	614.246	Downstream hub on bank, below birch tree.
TBM4.2	4	613.678	Upstream hub on bank.
BM40	4	619.739	Spike in tree on ledge. 15 m d/s of x-section on right of path to river from J.B. Little Brick yard
TBM5.1	5	614.079	Upstream hub on bank. (Not located, 12 Nov/90)
TBM5.2	5	614.271	Downstream hub on bank.
BM60	6	617.503	Spike in inside of trunk split in old tree, immed. above cross-section 6, approx. 4.5 m vertical up bank.
TBM6.1	6	613.96	Upstream hub on bank.
TBM6.2	6	613.606	Downstream hub on bank. (Not located, 12 Nov/90)
ASC98137		622.071	92 St, 100 A Ave. SW corner of intersection, 24 m S of 100 Ave, 8 m E of hockey rink.
ASC159244		617.911	87 ST, 102 Ave. E side of 87 St, 0.1 m W of E curb, 9.5 m S of N curb of 102 Ave.

Discharge in the North Saskatchewan River was obtained from preliminary hourly data collected by the Water Survey of Canada at stream gauging station 05DF001 (Water Survey of Canada, 1991). This is a recording stage-discharge station located approximately 1200 m downstream of the Rossdale Plant 3 outfall at the Low Level Bridge. The discharge at any station for any given time was obtained by allowing for the travel time from the location to the gauging station.

4.1.2 Tracer Study Methods

4.1.2.1 Injection

Rhodamine WT dye was selected as the tracer for these studies. It is highly soluble in water, has one of the lowest detection limits for fluorescent tracers, and is not subject to significant background interference (McCutcheon, 1989). The dye test served two functions: it provided information on the stream mixing characteristics in the reach of interest, and, served as a conservative datum from which chlorine decay rates could be compared. A complete discussion of river tracer studies using fluorescent dyes can be found in Church (1975), Feurestein and Selleck (1963) and McCutcheon (1989). The tracer study permits required by Alberta Environment are included in Appendix B.

Injection methods for both the E.L. Smith and Rossdale studies were similar. 20 L of a 2% (20 000 mg/L) solution of Rhodamine WT was prepared in the laboratory and transported to the injection site. Dye was stored on-site in a covered 100 L polyethylene reservoir along the riverbank. Figure 4.1 details the equipment at the injection site. A positive-displacement peristaltic pump was used to provide a discharge rate of 29 mL/min, which would provide a completely-mixed tracer concentration of 0.1 μg/L. The pump was calibrated in the laboratory prior to use, and was powered by a portable generator. One worker remained at the discharge site throughout the test to monitor the discharge rate and ensure that a continuous discharge was maintained. The flowrate was measured periodically throughout the duration of the tests, with no observed deviation.

From the pump, the dye solution flowed through tygon tubing to the discharge nozzle. At Rossdale, a discharge point located immediately downstream of the outfall and approximately 3 m from the bank was selected to provide the most accurate representation of the discharge after initial mixing within the river. A discharge point located 8 m off of the riverbank was selected as the most representative at E.L. Smith. This selection was later confirmed by visual inspection as the dye plume was at the midpoint of a lime centrate

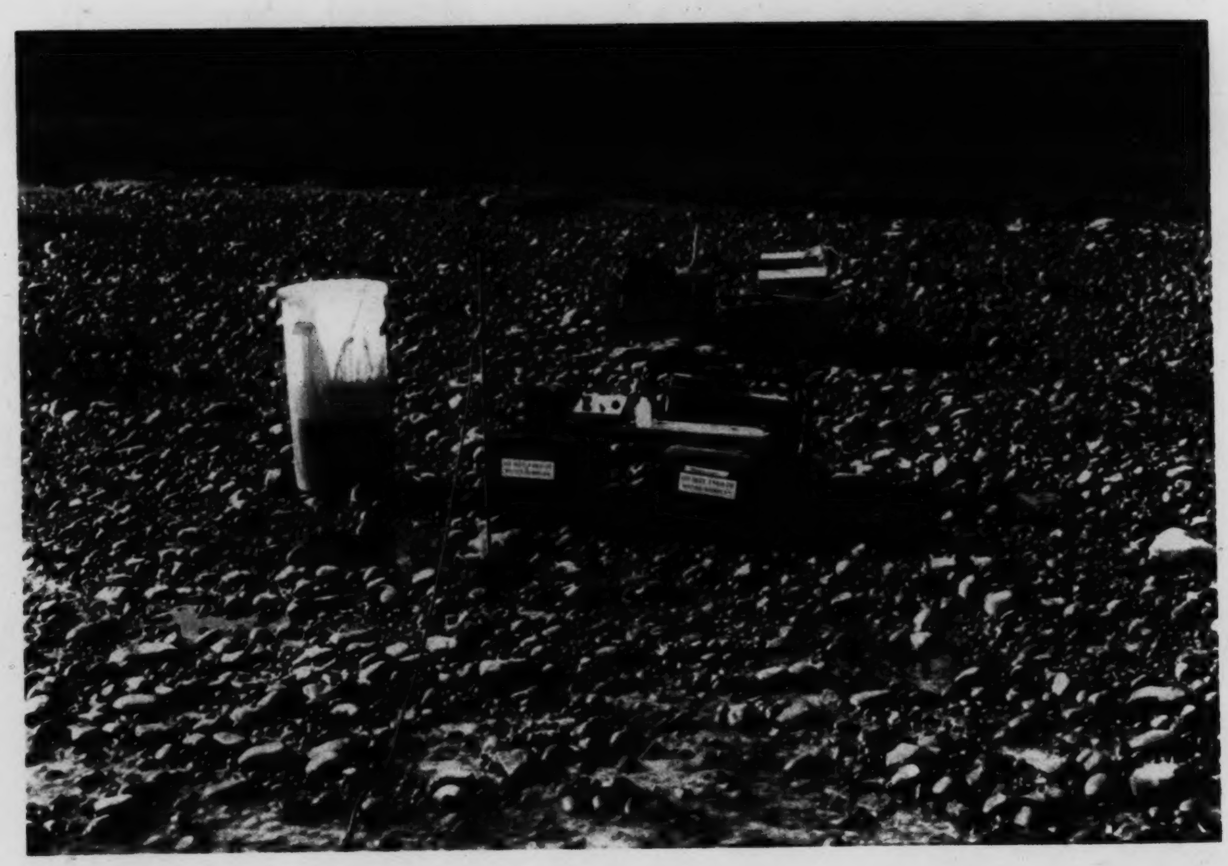


Figure 4.1 Rhodamine WT tracer injection system.

discharge plume. The dye was discharged from a 6 mm diameter stainless steel rod immersed approximately 100 mm beneath the water surface. The nozzle and tubing were anchored to a support driven into the river bed. Discharge velocities were comparable to the stream velocity in the region of the outlet, and the discharge behaved as a passive plume. Discharge and in-stream conditions for the dye tests are summarized in Table 4.2. Figure 4.2 shows the tracer plume at and immediately downstream of the injection site.

4.1.2.2 Sample Collection

Rhodamine WT sampling points at each cross section were selected to obtain a detailed transverse profile of the plume. The sample locations were choosen to provide good plume definition, with emphasis placed on obtaining samples near to the left bank, and with decreasing frequency approaching mid-channel. This was because the plume was expected to closely hug the left bank, with concentrations decreasing to background approaching the right bank. The maximum distance sampled off the left bank was increased at successive downstream stations to account for the greater lateral spread of the plume. The points sampled during each test are summarized in Table 4.3. A series of samples upstream from the injection points were also collected to provide information on background fluorescence within the North Saskatchewan.

Transverse distance across the channel was determined using a Topofil®, which provides a level of accuracy sufficient for most hydrographic surveys. The Topofil® was mounted onto the sampling side of the boat, where the off-shore distance could easily be read by the boat's pilot. The boat was slowly brought into position at the desired transverse distance, and was held in position parallel to the bank with the topofil line taut for sampling while the samples were obtained.

At each sample point, triplicate samples were collected in 125 mL Nalgene® polyethylene bottles from approximately 300 mm below the water surface. The samples were collected individually over a period of approximately 30 seconds to allow for an averaging of the effects of local concentration gradients caused by mixing phenomena. Samples were tagged with premarked labels and immediately placed in covered coolers to shield them from UV light. At the end of the sample collection, the coolers were transported back to the laboratory and stored at 4 °C until analyzed. Previous investigation into the use of polyethylene bottles for Rhodamine WT samples indicated that adsorption to the bottle surface would be negligible if samples were analyzed within 10 weeks (McCutcheon, 1989).

Table 4.2. Dye discharge conditions.

Parameter	Rossdale	E.L. Smith
Injection concentration (mg/L)	20 000	20 000
Injection flowrate (mL/min)	29.0	29.0
start time	10:00	10:00
finish time	18:15	19:00
total dye loading (mg)	287 100	313 200
estimated fully-mixed concentration (µg/L)	0.10	0.10

Table 4.3. Dye sample collection points.

Cross section	Rossdale Sampling points: distance from left bank (m)	E.L. Smith Sampling Points: distance from left bank (m)
1	2, 3, 4.4, 6.4, 10, 18	3, 4, 6, 7, 8, 9, 10, 11, 12, 15
2	2.4, 4.4, 8, 12, 16, 20, 28	3, 6, 9, 12, 15, 18, 21,24
3	3, 8, 12, 18, 24, 30, 40	3, 6, 9, 12, 16, 20, 24, 30
4	3, 6, 11, 16, 24, 32, 40, 50	3, 6, 9, 12, 16, 20, 24,30, 40
4	3, 6, 10, 16, 24, 32, 40, 50, 60, 75	3, 6, 9, 12, 16, 20, 24 ,30, 40, 50
6	3, 6, 10, 16, 24, 32, 40, 50, 60, 75	3, 6, 9, 12, 16, 20, 24, 30, 40, 50, 60, 80

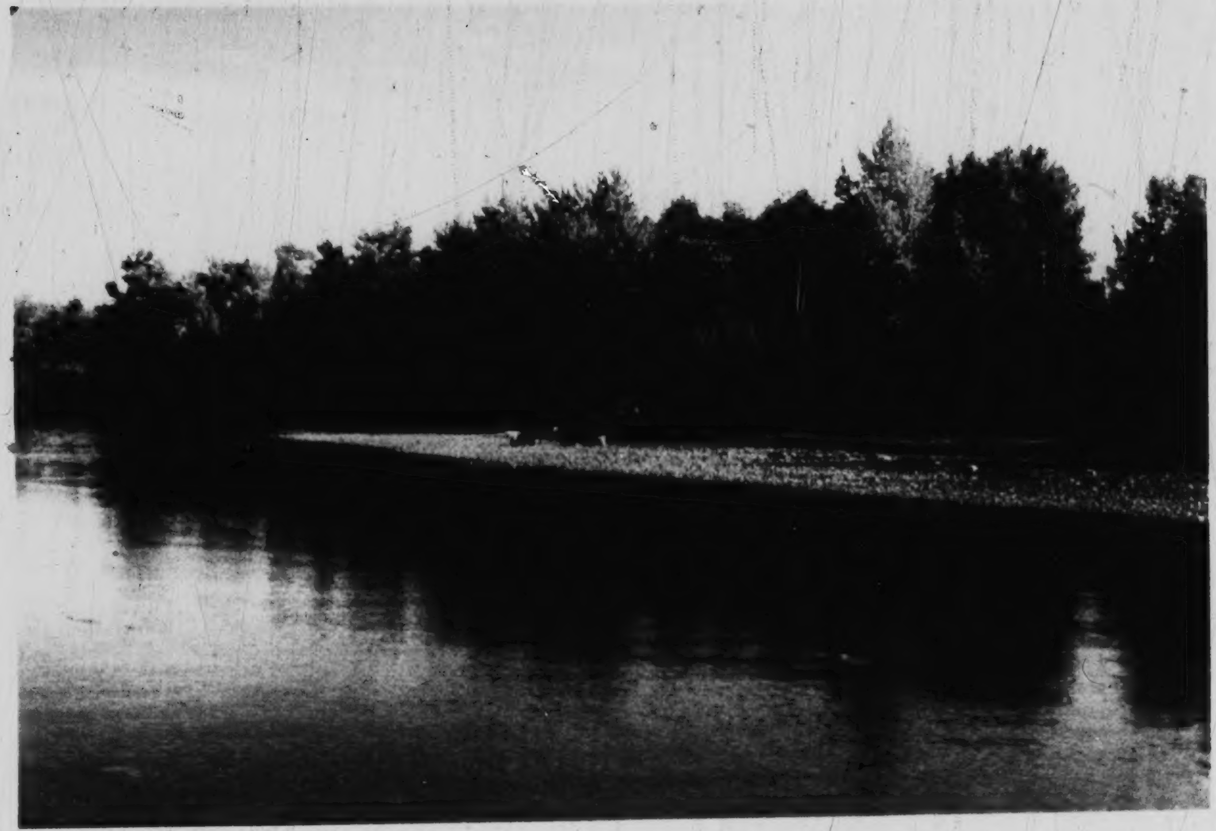


Figure 4.2 Rhodamine WT plume immediately downstream of the E.L. Smith Water Treatment Plant.

4.1.2.3 Rhodamine WT Analysis

All Rhodamine WT analyses were performed with a Turner Designs Model 10 Fluorometer. This instrument was calibrated using a two-stage linear calibration over the range of 0.007 µg/L to 100 µg/L (Appendix D). Samples at concentrations exceeding 100 µg/L were analysed by dilution. The analysis method was similar to those described by Church (1975), McCutcheon (1989) and Feurestein and Selleck (1963), which should be consulted for a detailed description of the theory and method of fluorometric tracer detection.

As Rhodamine fluorescence is very temperature sensitive, all samples were removed from cold storage and allowed to equilibrate to room temperature prior to analysis. Typical of late summer and fall periods, sediment concentrations within the river were very low. Although no data was available, the mean raw water turbidity was 14 NTU during the Rossdale study, and 4.2 NTU during the E.L. Smith test. The effects of excitation light absorbtion and scatter and dye sorption onto sediments present at these low concentrations would be expected to be negligible (McCutcheon, 1989).

Fluorescence readings were recorded for each sample and averaged to obtain a mean fluorescence value. Generally, results from the triplicate samples were very consistent, with replicate samples exhibiting a coefficient of variation of less than 4%. Rhodamine WT concentration was then calculated by substitution of the mean fluorescence value into the calibration equation. Actual concentrations were determined by subtracting background fluorescence concentrations.

4.1.3 Chlorine Study Methods

Field investigations of the distribution of residual chlorine downstream from Rossdale's Plant 3 outfall were conducted on September 6, 1990. Residual chlorine concentration profiles were determined at cross sections 1,2,3, and 4. An additional cross section, 1A, was also sampled to provide additional data on the plume. A similar test was conducted at E.L. Smith on September 26. Residual chlorine was measured at cross sections 1,2,3, and 4 during the day. In addition, a limited sampling of cross sections 3 and 4 was repeated at night to determine the effect of sunlight on chlorine decay.

4.1.3.1 Discharge Conditions

Discharge waters for the chlorine plume studies were obtained by routing output from the water treatment plants to waste instead of the reservoir. The discharge water used in the studies was final product water from the plants. Several limitations were present in obtaining these discharges for the studies. A period of approximately six hours was required to allow development of a steady state plume prior to the initiation of any sampling. It was also desirable to obtain the highest flowrate possible in order to closely simulate actual bypass conditions, and to provide sufficient chlorine to allow downstream detection. However, the maximum attainable discharge rate was limited as the plants were required to meet the normal demand required by other water users. The flowrates used were 32.4 ML/d at Rossdale and 32.5 ML/d at Smith. A summary of the discharge conditions for the chlorine plume tests is provided in Table 4.4.

Total chlorine residuals in the plant discharge waters were obtained from the operating records at the plants (City of Edmonton, 1990). These values were measured immediately after treatment. No provision for flow metering of the discharges was available, and estimates of the discharge flowrates were obtained through a water balance on the plants.

4.1.3.2 Sample Collection

A similar protocol to that used for dye sample collection was used for collection of residual chlorine samples. To eliminate chlorine consumption within the sample container, residual chlorine samples were collected headspace free in 250 mL chlorine-demand-free glass bottles. Chlorine-demand-free bottles were prepared according to Standard Method 4500-Cl C. (AWWA-APHA-WPCF, 1989).

The transverse locations for chlorine sample collection were determined interactively, based upon results from previously sampled points. Typically, at each cross section, samples were collected at 3 m intervals from the left bank to the distance where residual chlorine was no longer detectable. Table 4.5 lists the points sampled for each test.

4.1.3.2 Chlorine Analysis

In-stream chlorine residuals were measured by amperometric titration. As TRC concentrations within the discharge plume were expected to be present at levels ranging from near 2.0 mg/L near the outfall to less than 0.10 mg/L throughout much of it's

Table 4.4. Chlorinated Water Discharge Conditions.

Parameter	Rossdale	E.L. Smith
Q (ML/d)	32.4	32.5
mean total Cl_2 (mg/L)	2.12	2.06
temperature (°C)	17.0	13.0
discharge start time	06:00 Sept. 6	09:15 Sept. 27
discharge finish time	23:00 Sept. 6	01:00 Sept. 28

Table 4.5. Chlorine Sample Collection Points.

Cross section	Rossdale sampling points: distance from left bank (m)	E.L. Smith sampling points: distance from left bank (m)
1	2.4, 4, 4.4, 8, 11, 14	3, 6, 9, 10, 12, 15, 18, 21, 24
1A	3, 6, 12, 18	
2	2.4, 4, 10, 15, 20, 25	3, 6, 9, 12, 15, 18
3	3, 6, 9, 12, 18, 32	day: 3, 6, 9, 12, 15, 18, 21, 24 night: 6, 12
4	1, 4	day: 3, 6, 9, 12, 15, 18, 21, 24, 30 night: 3, 12, 18

distance, both the Amperometric Titration (Standard Method 4500-Cl D) and Low-Level Amperometric Titration Methods for Residual Chlorine (Standard Method 4500-Cl E) (APHA-AWWA-WPCF, 1989; Brooks and Seegert, 1979) were selected. The Low-Level Amperometric Titration Method is similar to the standard amperometric chlorine titration method, but uses a more dilute titrant and a graphical procedure to determine the endpoint. The Amperometric Titration Method is the current laboratory standard, and is the recommended method for measurement of chlorine residuals (Gordon et al., 1988: APHA-AWWA-WPCF, 1989). It is affected little by common oxidizing agents, turbidity, colour, or temperature variations. The Low-Level Amperometric Titration Method is recommended for detection and quantification of chlorine residuals below 0.2 mg/L, and is reported to allow measurement of chlorine concentrations as low as 10 µg/L (AWWA-APHA-WPCF, 1989). However, due to the low concentrations of the various species that may be present, it is unable to differentiate between the various forms of free and combined chlorine that may be present.

One modification was made to the procedure as described in Standard Methods. Sodium thiosulphate was substituted for phenylarsine oxide as the titrant. This substitution was made as past experience with the titrators had indicated that better performance could be obtained using sodium thiosulphate for residual determination at low chlorine levels. Sodium thiosulphate and phenylarsine oxide have been reported as interchangeable in the amperometric titration method for residual chlorine by Aieta et al. (1984). Standard solutions of 0.025 N and 0.0025 N $Na_2S_2O_3$ were prepared in the lab, according to the method specified in Standard Methods.

Total residual chlorine concentration was calculated using Equation 4.1.

$$\text{mg Cl as } Cl_2/L = \frac{V_t \times N \times 35450}{200} \qquad (4.1)$$

where V_t = titrant volume

N= titrant normality

Using the Low-Level Amperometric Titration Method, in-field detection limits for total residual chlorine of approximately 0.01 mg/L were achieved.

As it was expected that a rapid rate of decay of the chlorine residual would be observed in the field, and as no suitable method for sample preservation was available, TRC samples were identified immediately following collection. A mobile laboratory was established in one of the boats to allow in-field chlorine analysis. It consisted of two Wallace & Tiernan Series A-790 amperometric titrators, all necessary reagents, chlorine-demand-free rinse water, a portable generator for power, and various other required pieces of laboratory equipment. Figures 4.3 and 4.4 show the portable analysis station.

Immediately following sample collection, the bottles were delivered to the chlorine analysis station and were immediately titrated. Using the two independent titration stations, typical times from sample collection to completion of the analysis was on the order of 1 to 3 minutes.

4.1.4 Bacteriological Methods

A series of microbiological samples were collected at the same time as the chlorine plume was sampled. The objective was to determine the effect of residual chlorine on the in-stream bacterial population, and to determine whether any significant effect of the chlorine plume was noticed by the microbial population of the river over the short contact times encountered. The standard indicator organisms of total heterotrophs, total coliforms, and fecal coliforms were enumerated.

All microbial samples were collected by immersing sterile Whirl-Pak® bags into the river. Sampling locations are summarized in Table 4.6. Samples were collected from a depth of 50 to 100 mm, at the same transverse location, and immediately following collection of the chlorine samples. Approximately 10 mg of granular sodium thiosulphate was added to the sample to quench any remaining chlorine residual. The sample bags were sealed and stored in a dark cooler, and transported back to the lab for analysis.

Each sample was analyzed for total coliforms, fecal coliforms and total heterotrophs. Total coliforms were enumerated using the MPN Fermentation Technique (Standard Method 9221 B) (APHA-AWWA-WPCF, 1989). Fecal coliforms were analyzed by membrane filtration using Standard Method 9222 D, and total heterotrophs were analyzed by membrane filtration according to Standard Method 9215 D.

4.1.4 Benthic Chlorine Demand

In-situ benthic chlorine demand tests were conducted at the E.L. Smith Water Treatment Plant. The benthic demand was quantified using a batch benthic uptake chamber installed on the river bottom. The objective of these studies was to determine the rate of chlorine demand exerted on the water column by the benthic materials. The chamber used in these

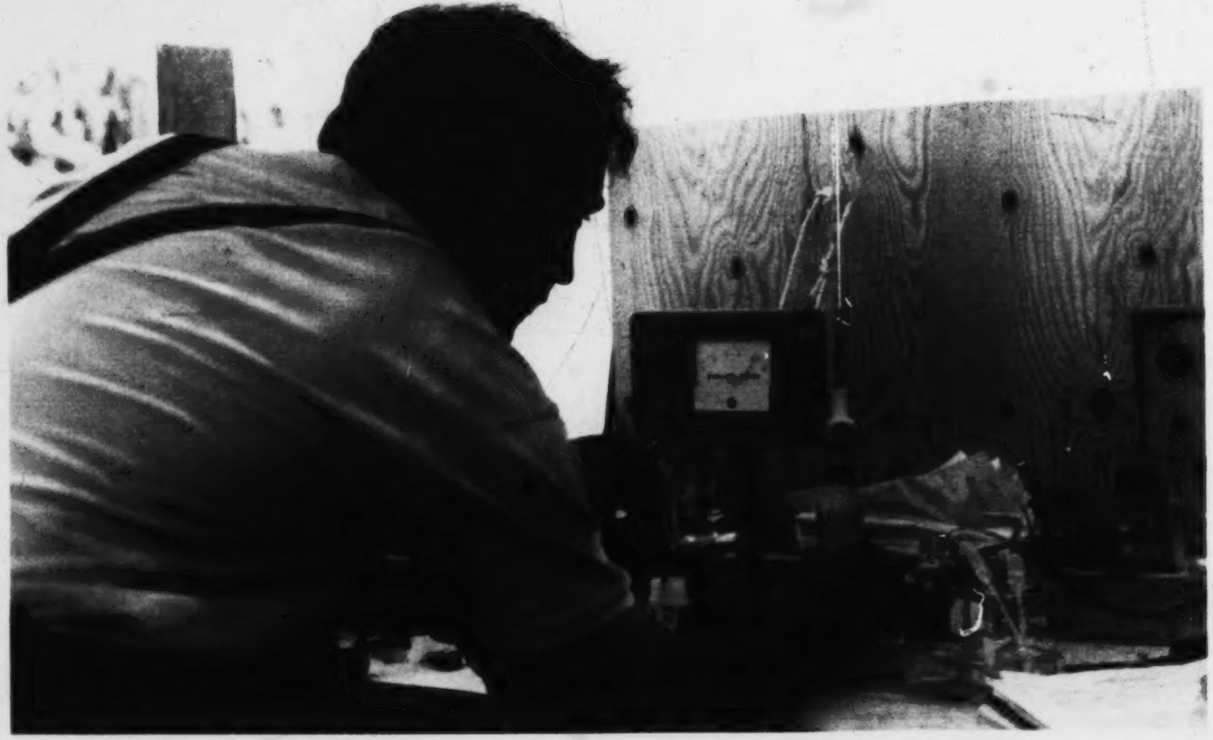


Figure 4.3 Field operation of amperometric titrators.

Figure 4.4 In-stream chlorine analysis downstream from the E.L. Smith Water Treatment Plant.

Table 4.6. Microbial sample collection points.

Cross section	Rossdale sampling points: distance from left bank (m)	E.L. Smith sampling points: distance from left bank (m)
1	3, 10, 12.4	3, 6, 9, 10, 12, 15, 18, 21
1A	3, 6, 12, 18	
2	2.4, 10, 15, 18	3, 6, 9, 12, 15, 18
3	3, 6, 9, 12, 14, 18	3, 6, 12 4, 21, 24
4	3	3, 6, 9, 12, 15, 18, 21,4 ,30

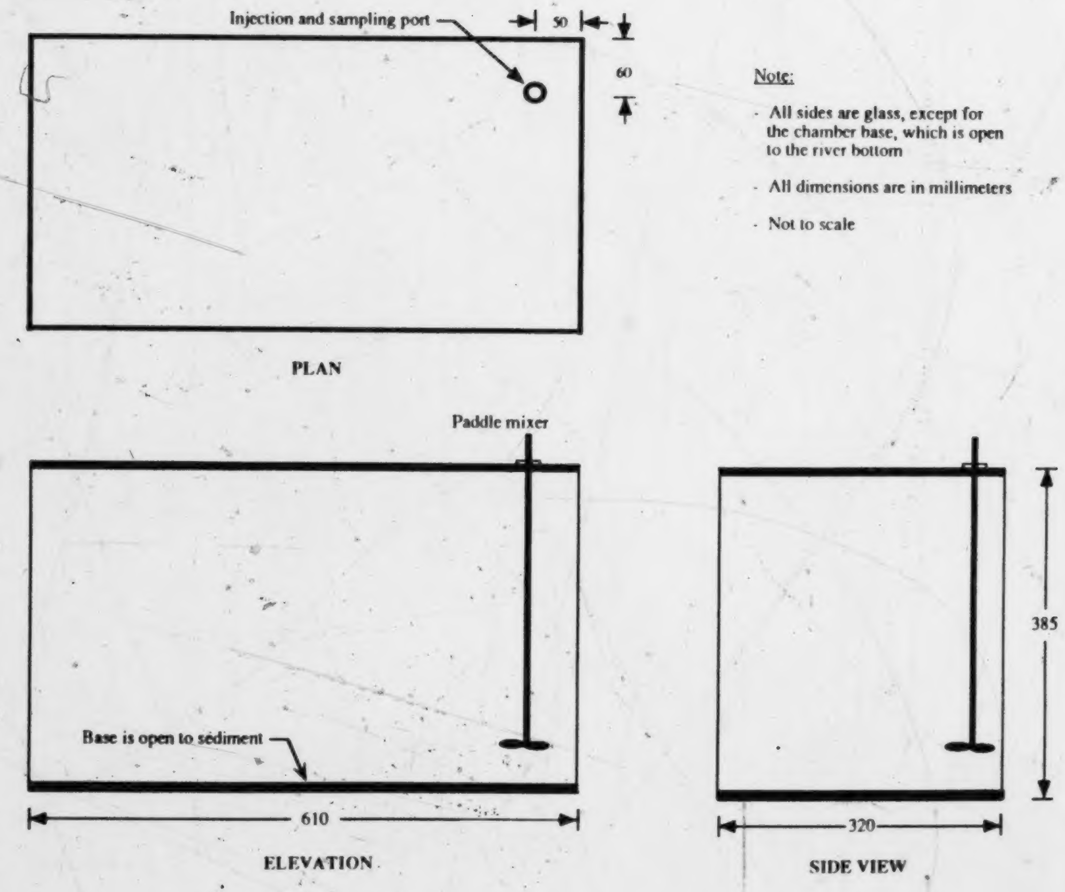
studies was a modified 75 L aquarium, used in an inverted position with the base open to the sediment. Several ports were added to the top to allow for sample extraction and mixing, while maintaining complete isolation from the river flow. A schematic of the apparatus is provided in Figure 4.5, and Figure 4.6 is a photograph showing sampling of the apparatus.

The chamber was placed in the river, in a flow depth approximately equivalent to the depth of the chamber. The bottom of the chamber was pressed into the river bed until a complete seal around the bottom was achieved, with the top was just below the water surface. All air within the apparatus was bled to atmosphere to reduce any volatilization of chlorine within the chamber. Chlorine, as NaOCl was injected with a syringe into the chamber through a rubber septa on one of the ports. The contents of the chamber were then immediately mixed using a manual paddle-stirrer. Using a 50 mL syringe, 200 mL samples were extracted at regular intervals through a sample port and analyzed for total chlorine residuals by amperometric titration as soon as practicable. No speciation of the chlorine residual was made, but as TRC was injected as free chlorine, it is possible that the residual was composed of both free and combined chlorine. Typical analysis times from collection to completion of the titration were less than 20 minutes. Regular, gentle mixing of the chamber contents was provided between sampling intervals.

4.2 Laboratory Investigations of Chlorine Decay

Laboratory investigations of the decay rates of chlorine in North Saskatchewan river water were conducted to determine the contribution of chlorine decay and reactions with other compounds present in the water matrix to the overall decay rate observed in the field. Samples of North Saskatchewan River water were obtained from the raw water intakes of both the E.L. Smith and Rossdale Water Treatment Plants. These were transported back to the lab at the University of Alberta, and either stored overnight or used immediately.

River water samples were placed into a 12 L capacity reaction and delivery tube. To reduce adsorption and reactions with the container materials, the reaction tube was made of stainless steel, and was isolated from the atmosphere with a floating teflon® cap. A schematic of the reaction tube is provided in Figure 4.7. As all materials were inert, and no light penetration or volatilization was allowed, any observed reduction in total chlorine residual concentration with time could be ascribed to time-dependent decay and reactions with constituents present within the water matrix.


Injection and sampling port
50
60
PLAN
Paddle mixer
Base is open to sediment
610
ELEVATION
385
320
SIDE VIEW

Note:

- All sides are glass, except for the chamber base, which is open to the river bottom
- All dimensions are in millimeters
- Not to scale

Figure 4.5 Benthic uptake apparatus.

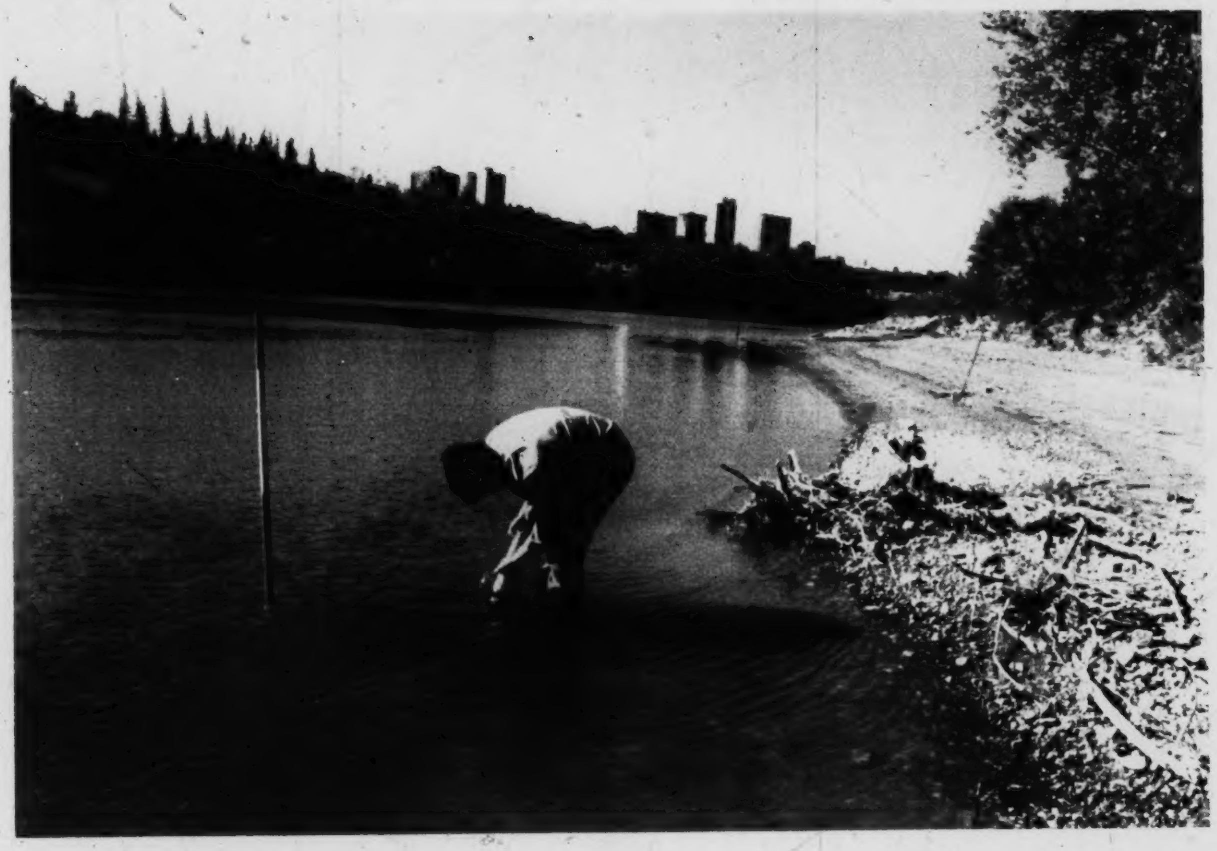
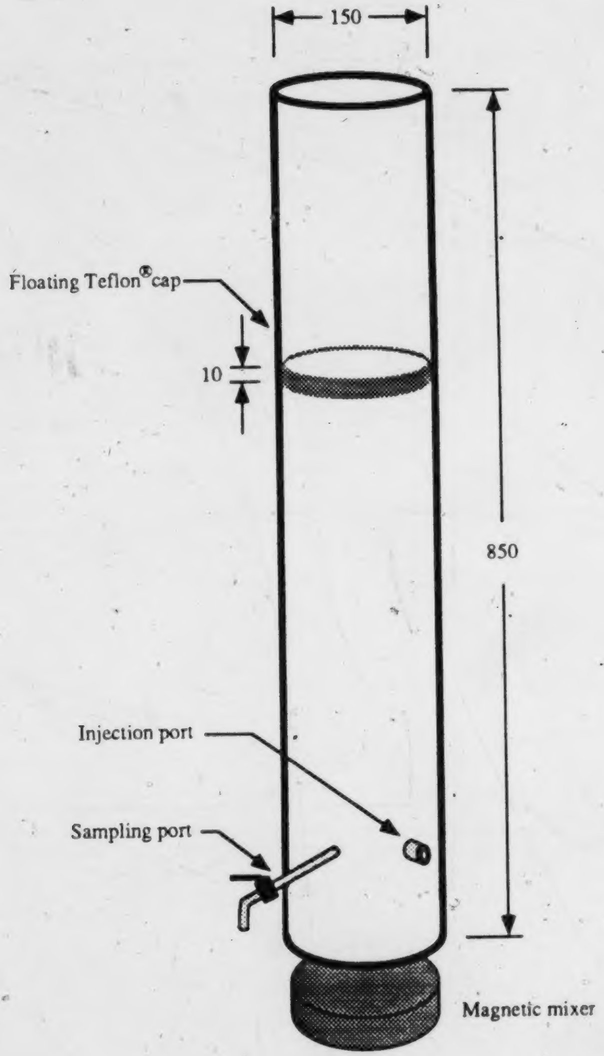


Figure 4.6 Sampling of the benthic uptake chamber.


150
850
Floating Teflon® cap
10
Injection port
Sampling port
Magnetic mixer

Note:

- All materials 316 stainless steel or Teflon
- 12.0 L capacity
- All dimensions in millimetres
- Not to scale

Figure 4.7 Chlorine decay reaction tube.

Sodium hypochlorite from a standardized solution was injected into the tube through a side port, and was immediately mixed with the contents of the tube by a Teflon® stir-bar and magnetic mixer. Samples were then extracted at regular intervals through a sampling port and analyzed by amperometric titration for total residual chlorine. No analysis to determine the speciation of the residual was made. The experiment was continued until residual chlorine concentrations dropped below the detection limit.

5.0 Site Description

5.1 General

The North Saskatchewan River through Edmonton is a major tributary in the Saskatchewan - Nelson river system. From its source in the Saskatchewan Glacier in the Columbia Icefields along the Alberta - British Columbia border, it flows eastward across central Alberta and Saskatchewan until it's confluence with the South Saskatchewan River near Prince Albert to form the Saskatchewan River. The Saskatchewan then flows into Lake Winnipeg, and eventually drains into Hudson Bay through the Nelson River. Major tributaries to the North Saskatchewan upstream of Edmonton include the Clearwater, Nordegg and Brazeau Rivers. Figure 5.1 shows major features of the watershed upstream of Edmonton, which comprises an area of 27,195 km^2 (Anderson et al., 1986).

Water quality in the North Saskatchewan is generally good relative to the Alberta Surface Water Quality Guidelines (Hrudey, 1986). A large proportion of the upstream watershed is uninhabited mountains and forests, with little municipal or industrial development, and few point sources of pollution. From Drayton Valley downstream, the percentage of agricultural land use increases. The major source of upstream pollution is runoff from forested and agricultural lands. Extensive summaries of the water quality in the North Saskatchewan around Edmonton have been prepared by Anderson et al. (1986) and Hrudey (1986).

The only known discharge of chlorine upstream of Edmonton is a chlorinated municipal sewage discharge from the town of Devon. Sewage at Devon is treated by primary clarification, with secondary treatment with a rotating biological contactor. Chlorine is used to disinfect the effluent prior to discharge to the river from a outfall along the south bank. As this plant is situated approximately 20 km upstream from E.L. Smith, and due to the small discharge rate, no background residual chlorine from this source would be expected at Edmonton; this was confirmed by background samples taken during the field program. No other sources of chlorine exist over the reach of interest for this study.

Flow in the North Saskatchewan has been regulated since 1973 by two dams, the Bighorn Dam, on the North Saskatchewan upstream of Nordegg, and the Brazeau Dam on the Brazeau River. These dams serve to attenuate the range of discharge extremes. Mean monthly flowrates since the construction of the above dams range from 113 m^3/s in January to 339 m^3/s in August (Environment Canada, 1989). A low flow analysis

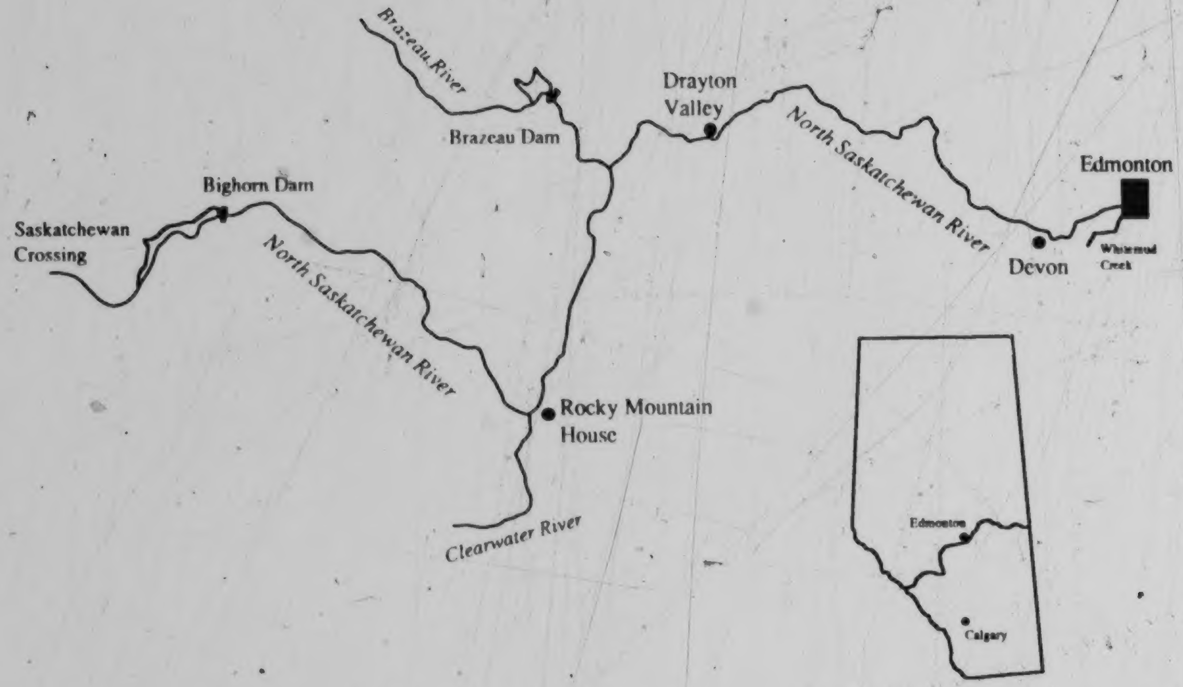

Brazeau River
Brazeau Dam
Drayton Valley
North Saskatchewan River
Edmonton
Whitemud Creek
Devon
Bighorn Dam
Saskatchewan Crossing
North Saskatchewan River
Rocky Mountain House
Clearwater River
Edmonton
Calgary

Figure 5.1 The North Saskatchewan River Upstream of Edmonton

conducted by Stanley and Smith (1991) using data collected since 1973 reported a 7Q10 value of 60 m^3/s. The historical data suggests that this flowrate will occur when an ice-cover exists on the river. Stanley and Smith (1991) suggested that a reasonable low flow value in open water conditions would be 80 m^3/s.

The North Saskatchewan River at Edmonton is in the form of an entrenched single channel with few mid-channel gravel bars. The channel pattern meanders irregularly, with point and side bars and several bends undercutting high cliffs of weathered sandstone. The average sinuosity through the reach of interest is approximately 1.40, with an average wavelength of 3.3 km (Kellerhals et al., 1972).

Bed materials through Edmonton are primarily quartzite gravels. Particle sizes range from a median of 0.23 to 0.25 mm, with a modal size of 16 mm (Anderson et al., 1986). Kellerhals et al. (1972) reported a grain size distribution for bed materials at Edmonton of 70 mm D_{90}, 40 mm D_{65}, and 31 mm D_{50}. The bed composition has been observed to vary significantly over short distances. A bed composed of fine materials is often seen just downstream from a predominantly gravel bed. The bed overlies a 4 to 5 m thick layer of gravel, which overlies bedrock of poorly consolidated shales and sandstones (Kellerhals et al., 1972). Anderson et al. (1986), Doyle and Thompson (1979) and Kellerhals et al. (1972) should be consulted for a more detailed description of the geomorphic characteristics of the North Saskatchewan through Edmonton.

The channel bed profile is apparently very stable. Alberta Environment reported that little change in the bed profile was observed between surveys conducted in 1912 and in the early 1950's (Anderson et al, 1986). It was also reported that no substantial change has been observed due to recent flood events. The reach is classified as being slightly unstable regarding lateral activity.

5.2 Rossdale Water Treatment Plant

The Rossdale Water Treatment Plant is actually composed of 3 independent treatment streams, known respectively as Plants 1, 2, and 3; each of which contributes to the total production. Standard North American water treatment practices are used at this plant. Treatment at Rossdale consists of adding alum, powdered activated carbon, ammonia and chlorine dioxide to the raw water as it enters the plant. To reduce the formation of chlorinated organics and reduce taste and odour problems chlorine dioxide is used at both water treatment plants as the initial disinfectant. The initial chemical addition and rapid mix is followed by flocculation, sedimentation, lime addition for softening, flocculation, settling of lime solids, addition of fluoride and chlorine, and filtration. Filter effluent is routed to on-site storage reservoirs prior to entering the distribution system . The three Rossdale plants have a combined nominal production of 200 ML/d.

Chlorinated effluent waters may be discharged from the Rossdale Water Treatment Plant from filter backwash operations or from plant bypass operation. The filter bypass operation is intermittent, with flows of 80 ML/d lasting for 8 to 10 minutes. Typically, backwash water is discharged 8 or 9 times per day. Discharges from each plant are routed to separate outfalls situated along the north bank of the river. Plant bypass operation is intended to prevent contaminated water in the treatment plants from reaching the distribution reservoirs without completely shutting down the affected plants. The plant can be by-passed either prior to or following the filters, just ahead of the reservoirs. The maximum plant bypass flowrate is 100 ML/d, which can be discharged through the 1220 mm tunnel outfall (Tritek Engineering Consultants Ltd., 1990). Figure 5.2 is a schematic of the Rossdale Plant, and shows the various outfall locations.

5.3 North Saskatchewan River at Rossdale Water Treatment Plant

The reach of the North Saskatchewan of interest for the Rossdale field investigations comprised an area extending from just upstream of the Rossdale Water Treatment Plant to the Capilano Bridge approximately 5 km downstream. An aerial photo of this region, showing cross section locations, is provided in Figure 5.3.

A survey of the above area was conducted on August 31, 1990. A series of six cross sections were established at distances of 110, 640, 1400, 2370, 3420, and 4520 m downstream from the plant 3 outfall. Downstream distances were determined by locating the cross sections on 1:5000 aerial photographs and scaling the distance along the channel centre. Depth soundings were made at these cross sections, and benchmarks were established on September 4, 1990. Cross-sectional profiles and calculated flow distributions for the above cross sections are provided in Appendix A. Table 5.1 provides a summary of channel geometry and hydraulic properties as found on September 4, 1990.

An additional cross section, 1A, at 300 m, was established during the chlorine plume test to obtain additional chlorine data. No soundings were made at this section, and where required, its profile was synthesized using several manual depth measurements and averages of the geometry at cross sections 1 and 2.

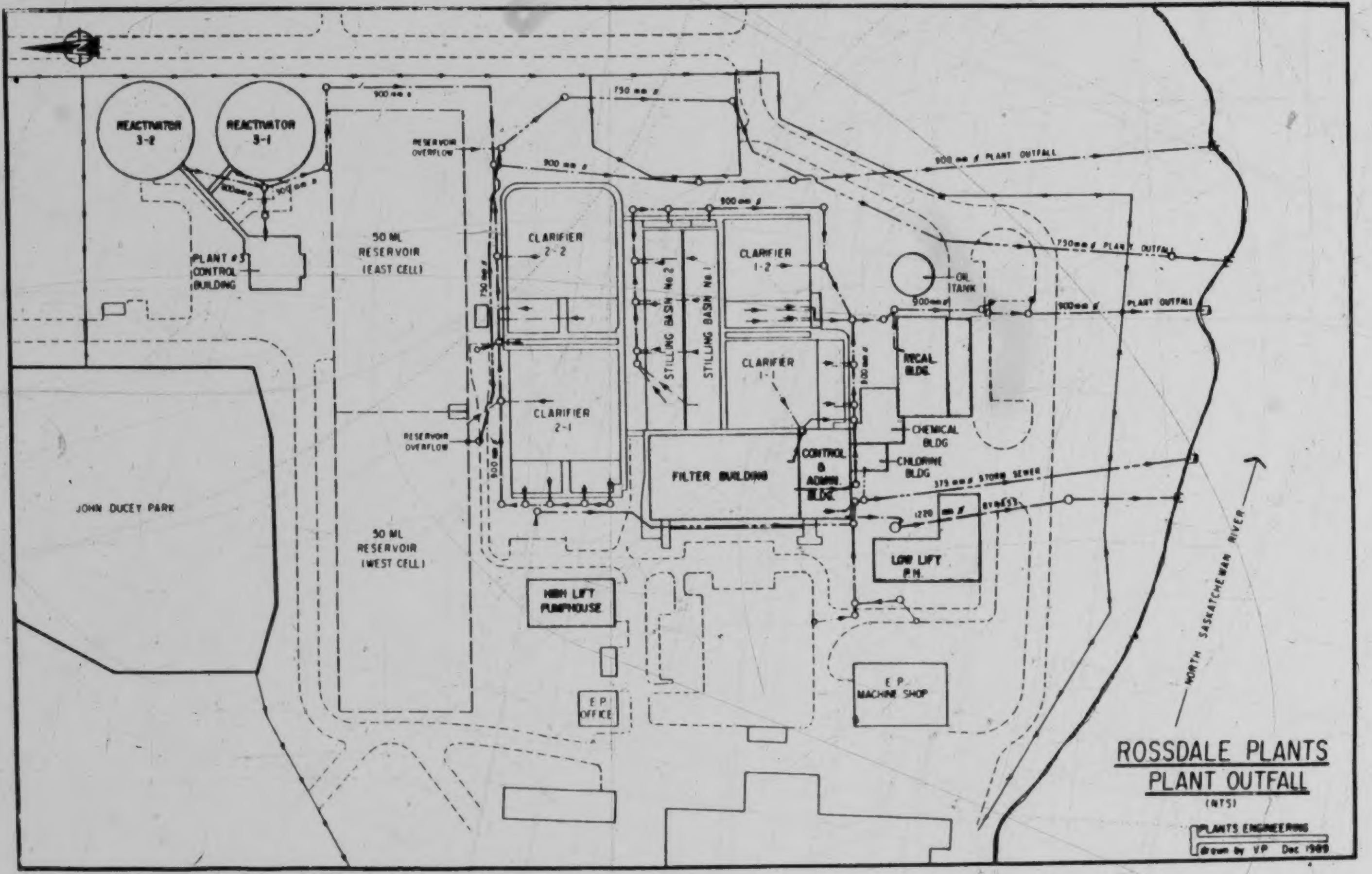

N
REACTIVATOR 3-2
REACTIVATOR 3-1
PLANT #3 CONTROL BUILDING
900 mm ø
750 mm ø
RESERVOIR OVERFLOW
50 ML RESERVOIR (EAST CELL)
50 ML RESERVOIR (WEST CELL)
JOHN DUCEY PARK
CLARIFIER 2-2
CLARIFIER 2-1
STILLING BASIN No 2
STILLING BASIN No 1
CLARIFIER 1-2
CLARIFIER 1-1
FILTER BUILDING
CONTROL & ADMIN. BLDG.
OIL TANK
RECAL BLDG
CHEMICAL BLDG
CHLORINE BLDG
900 mm ø PLANT OUTFALL
750 mm ø PLANT OUTFALL
900 mm ø PLANT OUTFALL
375 mm ø STORM SEWER
1220 mm ø BYPASS
LOW LIFT P.H.
HIGH LIFT PUMPHOUSE
E.P. OFFICE
E.P. MACHINE SHOP
NORTH SASKATCHEWAN RIVER
ROSSDALE PLANTS
PLANT OUTFALL
(NTS)
PLANTS ENGINEERING
Drawn by VP Dec 1989

Figure 5.2 Site diagram of the Rossdale Water Treatment Plant.

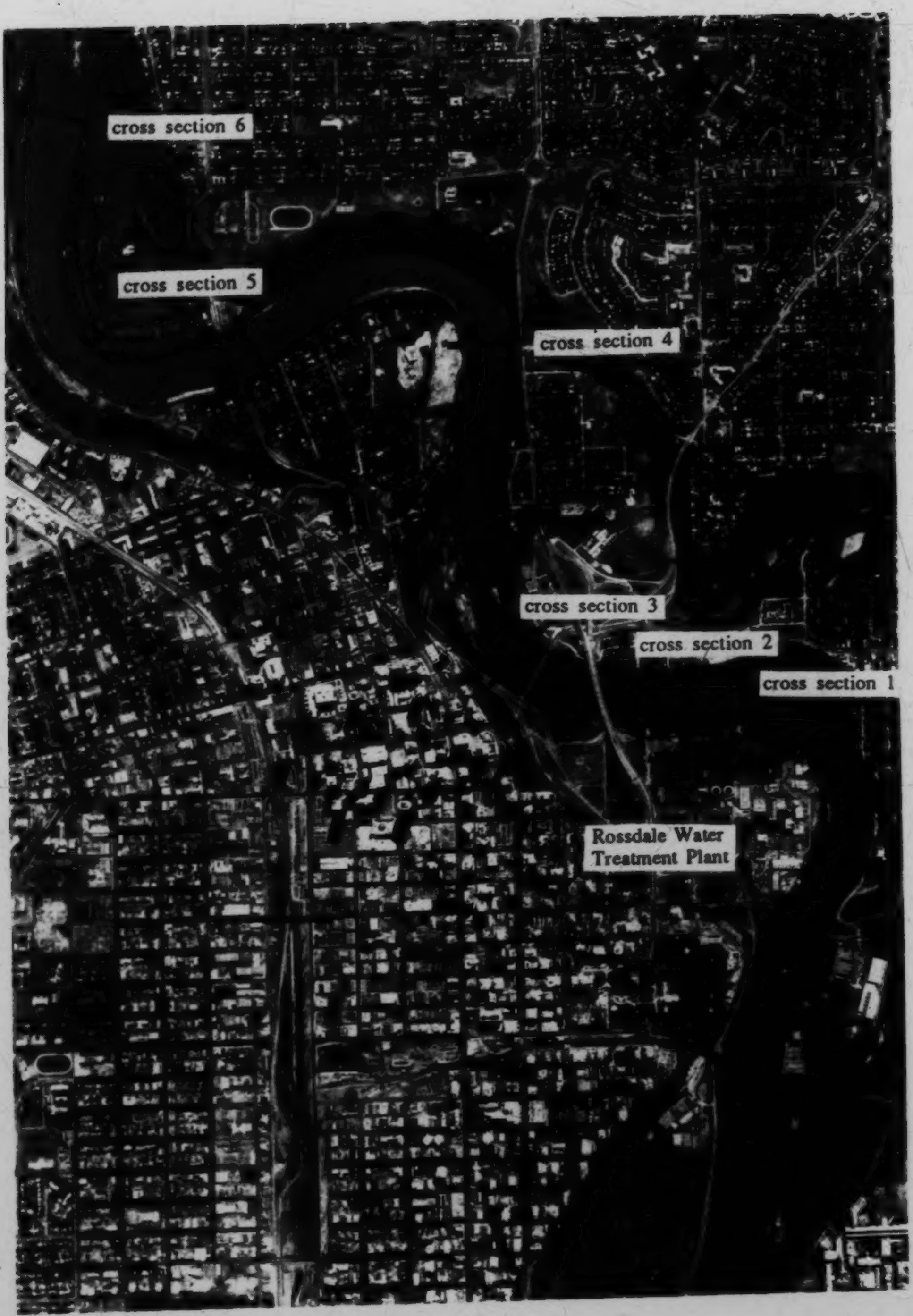

cross section 6
cross section 5
cross section 4
cross section 3
cross section 2
cross section 1
Rossdale Water Treatment Plant

Figure 5.3 Aerial photo of the North Saskatchewan River downstream from the Rossdale Water Treatment Plant (1:25000).

Table 5.1 Hydraulic Properties of North Saskatchewan River downstream of Rossdale Water Treatment Plant (Sept 4/90)

Cross section	Downstream distance (m)	B (m)	H (m)	U (m/s)	S	u* (m/s)
1	112	130	2.31	0.701	0.000406	0.096
2	637	167	1.19	1.086	0.000269	0.056
3	1402	140	1.68	0.89	0.000234	0.062
4	2367	180	1.48	0.755	0.000055	0.028
5	3422	168	1.69	0.686	0.000358	0.077
6	4520	164	1.4	0.832		

5.4 E.L. Smith Water Treatment Plant

The E.L. Smith Water Treatment Plant is a more modern plant, located along the north river bank approximately 17 km upstream from the Rossdale Plant. Its treatment scheme consists of addition of chlorine dioxide and ammonia, alum clarification in upflow clarifiers, lime softening in upflow clarifiers, secondary disinfection with chloramines, and filtration trough dual-media anthracite sand filters. There is provision for the addition of powdered activated carbon and activated silica. The nominal production capacity of the E.L. Smith plant is currently 200 ML/d.

Chlorinated waters from E.L. Smith are also discharged from plant bypass and filter backwash procedures. The backwash flowrate at Smith is 120 ML/d, with a frequency of about 6 times per day. The discharge can either be routed through a bank outfall, or to a diffuser located in the rivers centre (Figure 5.4). The maximum plant bypass flow at Smith is 140 ML/d, and is routed through the bank outfall.

5.5 North Saskatchewan River at E.L. Smith Water Treatment Plant

The reach of the North Saskatchewan of interest for the E.L. Smith field investigations comprised an area extending from just upstream of the Water Treatment Plant to a point approximately 3.1 km downstream. In this distance, the river travels around Terwillegar Park, with a relatively severe bend causing the flow to change direction by more than 180° over this short distance. An aerial photo of this region showing the location of each cross section is provided in Figure 5.5.

A survey of the above area was conducted on September 25, 1990. A series of six cross sections were established at distances of 125, 465, 1270, 1750, 2445, and 3100 m downstream from the outfall. Downstream distances were determined using the same method employed at Rossdale. Depth soundings were made at these cross sections, and benchmarks were established on September 25, 1990. Cross-sectional profiles and the associated flow distributions for each cross section are also provided in Appendix A. Table 5.2 provides a summary of channel geometry and hydraulic properties as found on September 25, 1990.

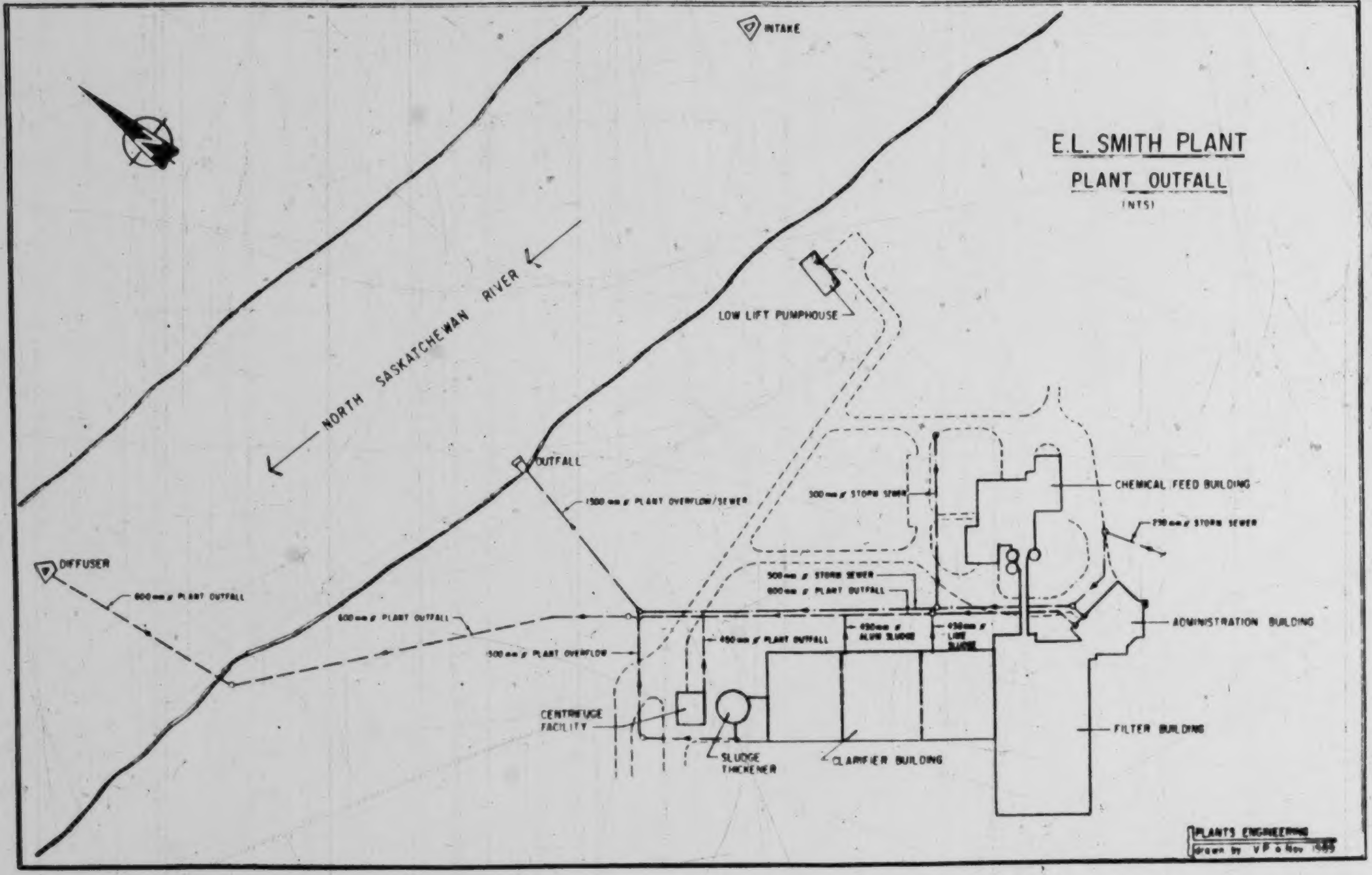

E.L. SMITH PLANT
PLANT OUTFALL
(NTS)
INTAKE
NORTH SASKATCHEWAN RIVER
LOW LIFT PUMPHOUSE
OUTFALL
DIFFUSER
1500 mm ø PLANT OVERFLOW/SEWER
600 mm ø PLANT OUTFALL
600 mm ø PLANT OUTFALL
500 mm ø PLANT OVERFLOW
300 mm ø STORM SEWER
500 mm ø STORM SEWER
600 mm ø PLANT OUTFALL
450 mm ø PLANT OUTFALL
450 mm ø ALUM SLUDGE
450 mm ø LIME SLUDGE
250 mm ø STORM SEWER
CHEMICAL FEED BUILDING
ADMINISTRATION BUILDING
FILTER BUILDING
CLARIFIER BUILDING
SLUDGE THICKENER
CENTRIFUGE FACILITY
PLANTS ENGINEERING
drawn by V P o Nov 1985

Figure 5.4 Site diagram of the E.L. Smith Water Treatment Plant.

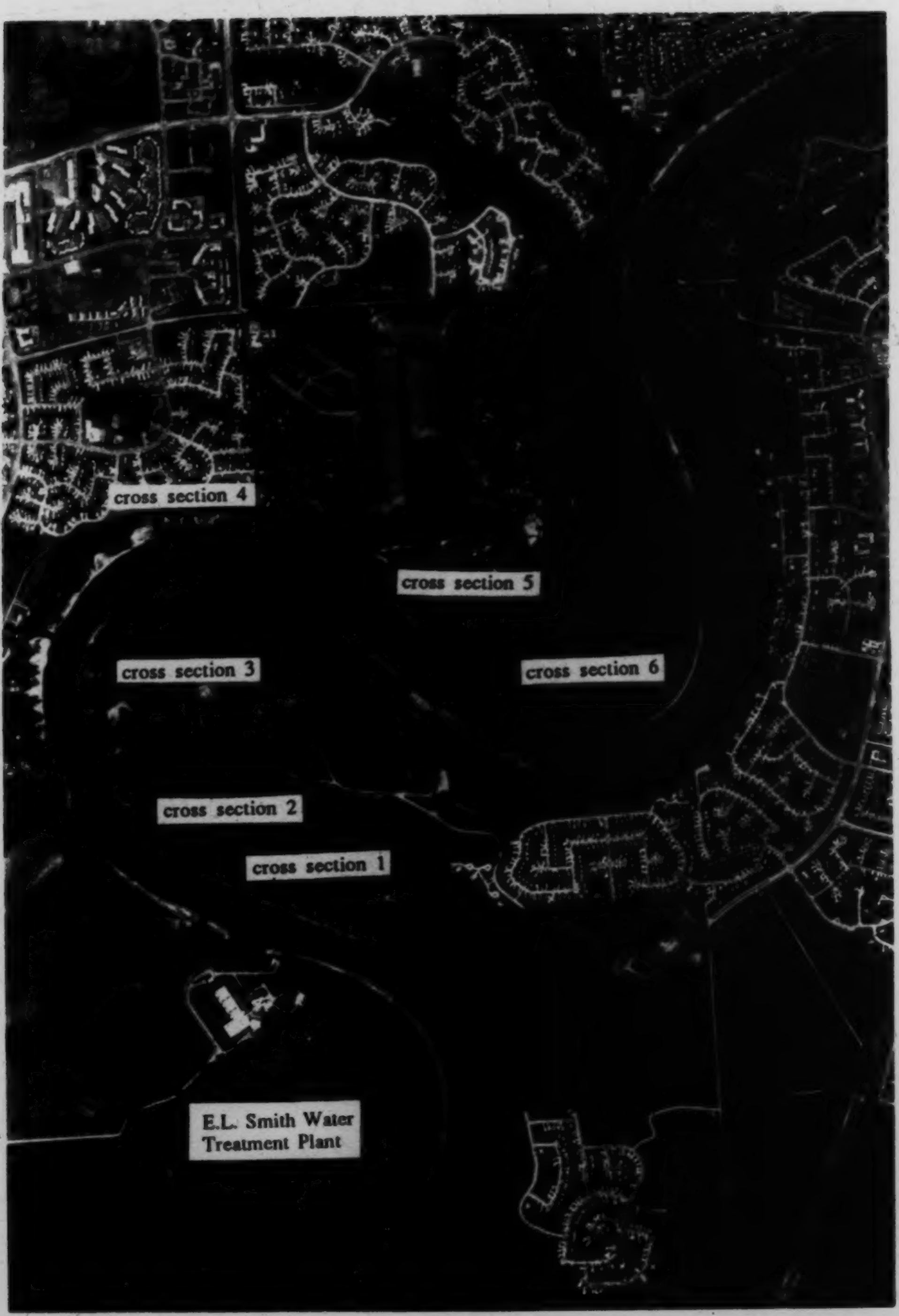

cross section 4
cross section 5
cross section 3
cross section 6
cross section 2
cross section 1
E.L. Smith Water Treatment Plant

Figure 5.5 Aerial photo of the North Saskatchewan River downstream from the E.L. Smith Water Treatment Plant (1:25000).

Table 5.2 Hydraulic Properties of North Saskatchewan River downstream of E.L. Smith Water Treatment Plant (Sept 25/90)

Cross section	Downstream distance (m)	B (m)	H (m)	U (m/s)	S	u* (m/s)
1	125	131	0.94	1.167	0.000704	0.082
2	465	142	1.61	0.630	0.000074	0.035
3	1270	132	2.40	0.456	0.000241	0.076
4	1750	160	1.29	0.697	0.000845	0.085
5	2445	160	1.04	0.868	0.000928	0.016
6	3100	145	1.00	0.995		

6.0 Results

Observations and results from the field studies conducted downstream of the Rossdale and E.L. Smith Water Treatment Plants are presented in the following section. Rhodamine WT data, chlorine distribution within the effluent plume, and microbiological distributions within the plume were conducted downstream of each plant. Studies of the benthic uptake rates for residual chlorine were also performed at the E.L. Smith plant. In addition to the field program, laboratory studies of chlorine decay within North Saskatchewan River water were performed to obtain estimates of the rate of decay of TRC due to chemical decay and reactions. This section provides a compilation of the collected data, along with a discussion of any assumptions required to obtain the data. Data interpretation and analysis is reserved for discussion in Section 7.0.

6.1 Rossdale Water Treatment Plant Field Study

Results from the field investigations at the Rossdale Water Treatment Plant are presented below. The dye test was conducted on September 5, 1990, with the chlorine plume test following the next day. The mean discharge in the North Saskatchewan over the study period was 196.6 m^3/s during the tracer study, and 196.8 m^3/s during the chlorine study.

6.1.1 Rhodamine WT Tracer Test

Results from the Rhodamine WT tracer tests are summarized below. Raw data, and summary statistics for individual sample locations is provided in Appendix C. Inspection of the brief statistical analysis provided in Appendix C indicates that the triplicate samples usually produced reproducible results. Generally, as the sampling progressed downstream, a greater precision was observed within each replicate group of samples. The mean coefficient of variation's, calculated as the average of the individual replicate sample coefficients of variation were, 44.7, 6.25, 44.3, 6.19, 3.6 and 5.73% from cross section 1 to 6 respectively. The scatter observed at the upstream cross sections can likely be attributed to the variable hydrography along this section, which produced several eddies and dead zones in which concentrated pockets of dye can be formed.

Observed tracer profiles across each of the established cross-sections are shown in Figures 6.1a and 6.1b. The same data, presented in a dimensionless form, is provided in Figures 6.2a to 6.2c.

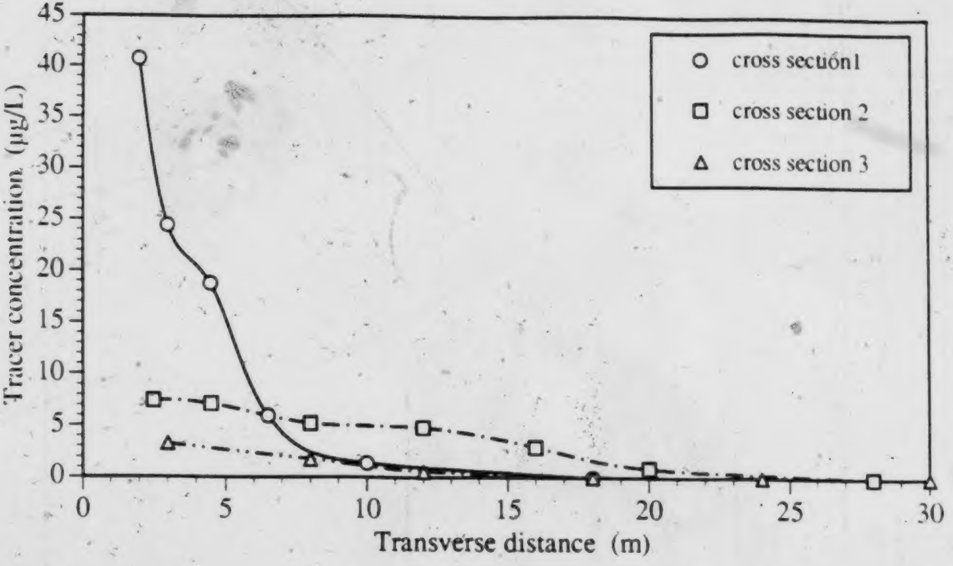


Figure 6.1a Rhodamine WT tracer profile: Rossdale cross sections 1 to 3.

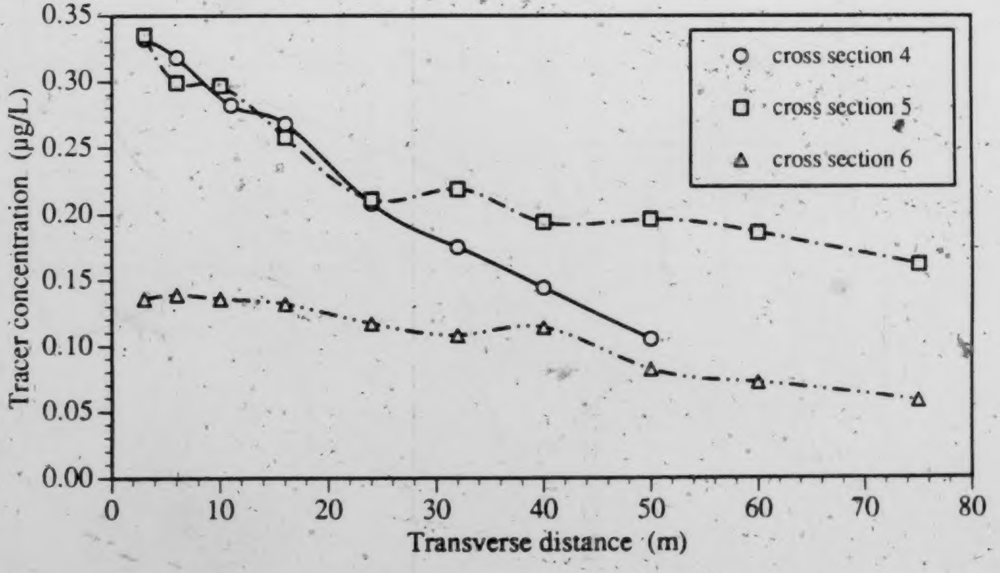


Figure 6.1b Rhodamine WT tracer profile: Rossdale cross sections 4 to 6.

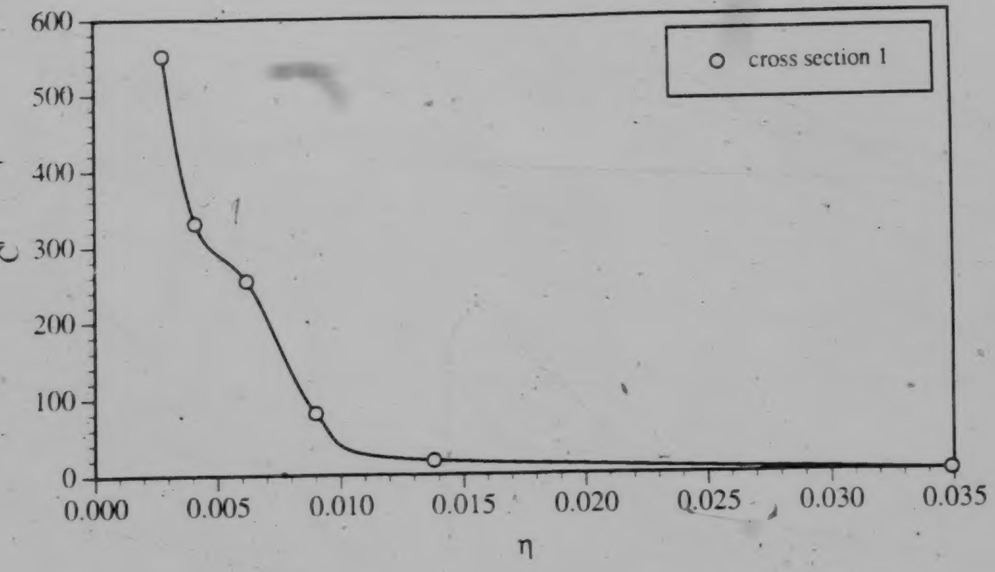


Figure 6.2a Dimensionless tracer profile: Rossdale cross section 1.

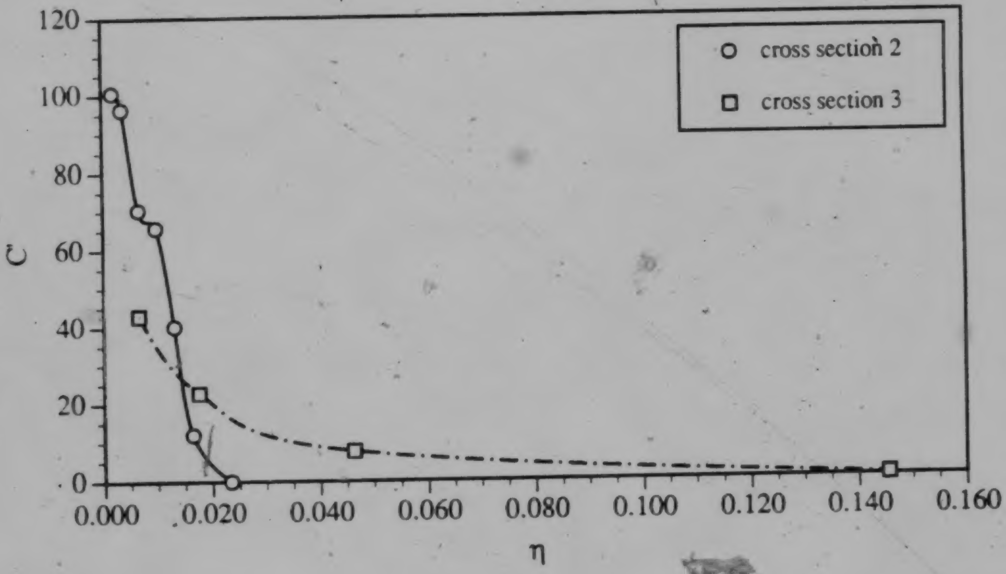


Figure 6.2b Dimensionlesss tracer profiles: Rossdale cross sections 2 and 3.

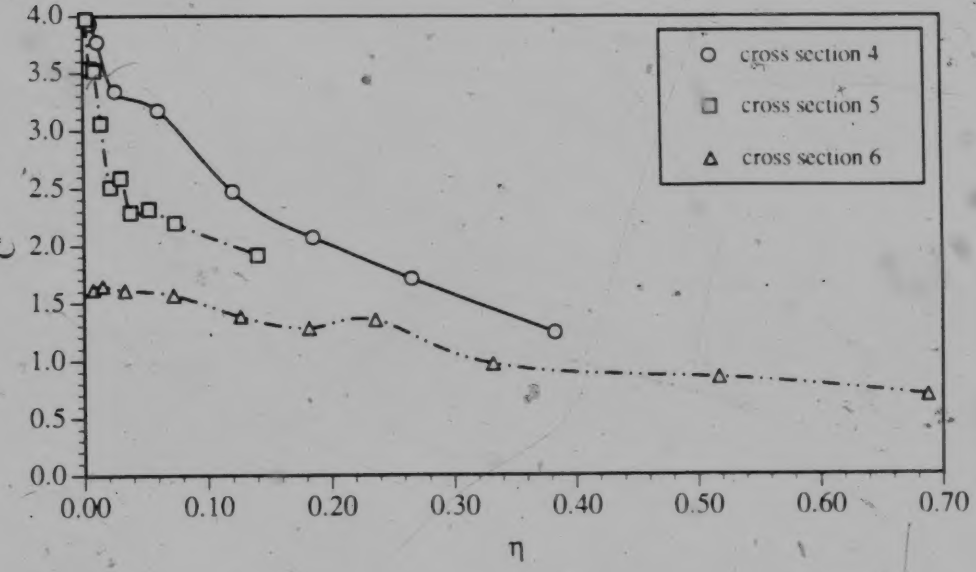


Figure 6.2c Dimensionless tracer profiles: Rossdale cross sections 4 to 6.

6.1.1.1 Mass Balance Analysis

To determine whether the dye was behaving as a conservative tracer, an initial mass balance on the tracer flux at downstream cross sections was conducted using local velocity predictions generated by the program TRSMIX.DV. TRSMIX.DV proportions the total flow in the channel into streamtubes using cross-sectional geometry and the Manning resistance equation. Use of this data in the mass balance indicated very poor recoveries, with as little as 20% of the predicted tracer mass recovered at some cross sections. Rhodamine WT is generally considered to be a conservative tracer, and very little loss would be expected in the short distances and travel times involved in this study (McCutcheon, 1989). Comparison of local velocities as predicted by TRSMIX.DV with velocity measurements obtained at each cross section indicated that the TRSMIX.DV predictions were not providing good velocity estimates along the near-bank zone. However, the quality of the estimates were quite acceptable within the main body of the flow.

As little tracer loss would normally be expected over the conditions found in this study, the apparent tracer loss was attributed to inaccuracies in the velocity estimates used in the initial flux calculations. The local velocities generated by TRSMIX.DV were adjusted by the method described below to provide a more representative description of the actual hydraulic conditions along the near-bank zone.

TRSMIX.DV proportions the flow across the given cross-sectional boundaries using the local resistance equation recommended by Beltaos (1978).

$$\frac{u}{U} \sim \left(\frac{h}{H}\right)^{a} \tag{6.1}$$

where u is the depth-averaged local velocity, U the mean cross-sectional velocity, h the depth at the vertical, and H the mean cross-sectional depth. The above equation can be derived from Manning's equation, with a = 0.67.

To determine whether Equation 6.1, with the Manning exponent 0.67, was the most appropriate for describing velocity distributions in the North Saskatchewan, a comparison of observed u/U vs h/H data was plotted in Figure 6.3. The distribution as predicted by Equation 6.1 is also shown. Although there is a considerable amount of scatter, it appears that use of Equation 6.1 with the Manning exponent 0.67 provides a reasonable

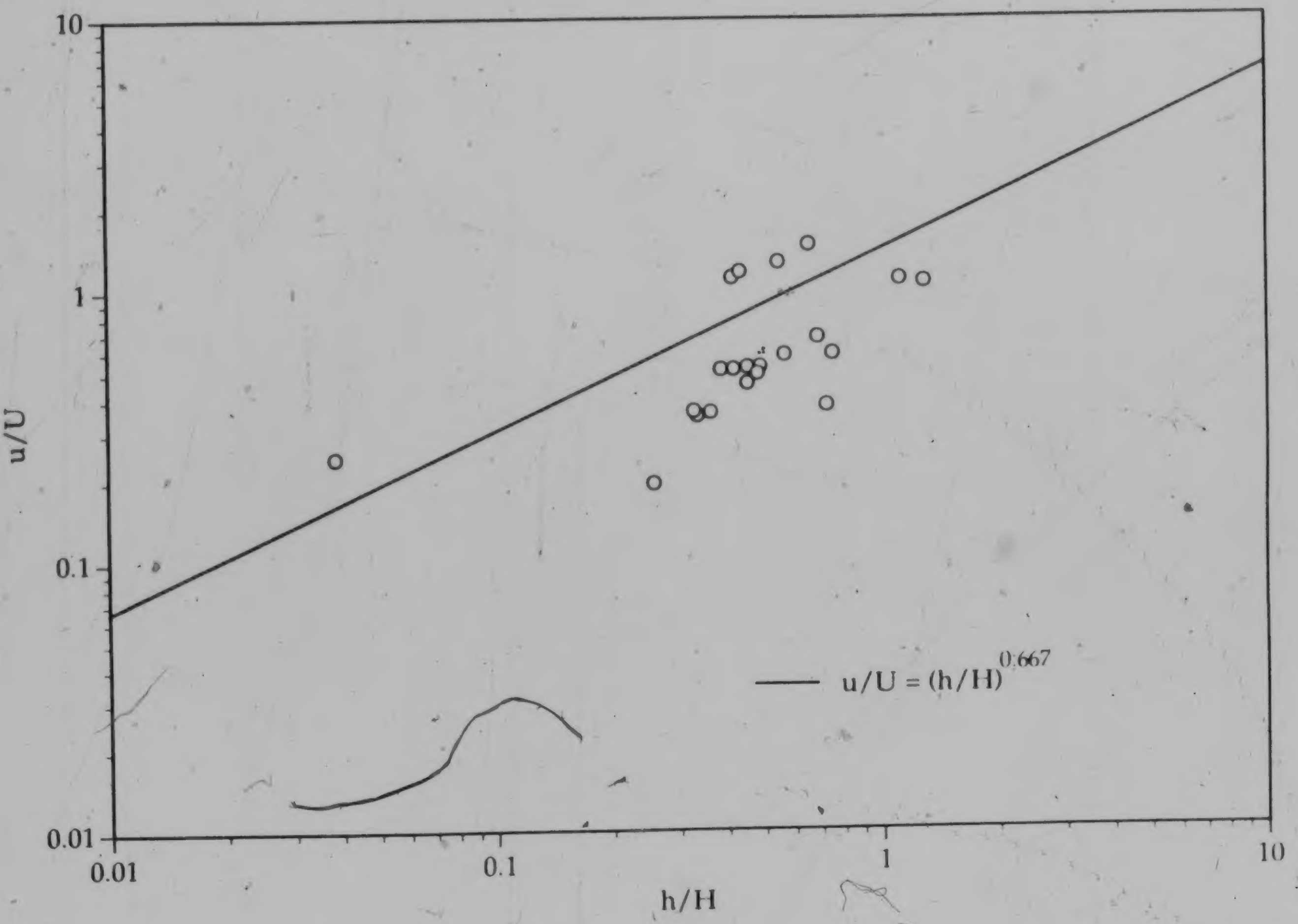


Figure 6.3 Velocity - depth correlation for discrete locations vs. mean channel properties.

approximation of the local velocities based on the given information. A similar conclusion was made by Putz (1983) in a mixing study on the Slave River. Local velocity estimates predicted by TRSMIX.DV would therefore be expected to be generally valid. Beltaos (1978) suggested that the exception to this may be along the near-bank zone, where changes in channel geometry can induce local velocity variations such as dead-zones and eddy areas that may cause considerable variations in local velocities from those predicted by Equation 6.1.

To obtain a more accurate estimate of flow velocities along the near-bank zone, the predicted flow distributions were plotted against velocity profiles measured in the field. The velocity profiles used in the mass balance, and in subsequent modelling were obtained by fitting a curve through the observed data points along the bank, and graphically merging this line with the predicted values as the mean flow area was approached. As previously stated, good agreement was obtained between measured and predicted values as the channel centre was approached. This procedure had a negligible impact on the flow distribution as only slight velocity corrections were made over a small proportion of η, however, it greatly improved the calculated dye recoveries at each cross section.

Using the above procedure, the mass balance was recalculated using the corrected velocity profiles. Recoveries from cross sections 2 to 6 are reported in Table 6.1. No attempt at a mass balance calculation was made for cross section 1 as the plume occupied too little of the total flow to obtain reliable estimates of the local flow parameters. Based upon steady-state input conditions, the predicted dye flux at any section across the river was 14.94 g/s. The percentage dye recovery was calculated based on this figure. As evident from Table 6.1, the amount of dye recovered varied from section to section, but was similar to results reported by previous researchers (Putz, 1983, Holley and Abraham, 1973). The observed variations in recovery are probably not due to actual losses, but instead, may have been due to errors in the channel geometry and flow property estimates. Due to the direct relationship between the two parameters, a 15% error in velocity estimates or channel cross sectional area will result in a 15% error in reported mass recovery.

The very low recoveries observed at cross section 5 can be explained by consideration of the channel geometry. Samples were collected up to 75 m off the north bank, representing almost 50% of the total channel width, but only 20% of the total streamflow was contained within this distance. Consequently, a significant amount of dye was present in the plume tail beyond the outermost sample point and yet was neither sampled nor accounted for in the mass balance.

Table 6.1. Rhodamine WT tracer mass balance.

Cross section	tracer flux (g/s)	Tracer recovery (%)
2	13.39	89.6
3	11.04	73.9
4	12.46	83.4
5	7.42	49.7
6	15.01	100.5

Recovery of 100.5% of the dye at cross section 6 also tends to support the conclusion that no significant dye loss occurred. At this, the furthest downstream cross section, the plume had spread to the maximum extent observed, and the sensitivity of the mass balance calculation to local velocity or geometry errors was reduced. Consequently, confidence in the calculated mass flux would be highest at cross section 6.

6.1.1.2 Transverse Mixing Coefficient Determination

The transverse mixing coefficient (E_z) for each section of the reach downstream from Rossdale was determined numerically using the program TRSMIX. The model output conditions, and all input parameters except the mixing coefficients were known. Values for E_z could therefore be obtained by comparison of field tracer data with model output using different mixing coefficients. As detailed measurements of the channel geometry and hydrography were available, this method was considered superior to available analytical methods, such as the method of moments. Yotsukura and Cobb (1972), Yotsukura and Sayre (1976), Lau and Krishnappen (1985) and Putz (1984) have used this method with success.

Numerical simulation of the plume immediately downstream from the discharge was impossible as the plume would not be completely mixed in the vertical for 50 to 100 m. An analytical solution for a point source input was used to generate the tracer profile at a downstream distance of 60 m. It was desirable to begin the numerical solution as near as possible to the injection point, as the analytical solution was unable to model a non-conservative pollutant. This would therefore minimize the distance over which decay was neglected during analysis of the chlorine plume. A start point for the numerical solution of 60 m was judged to provide a reasonable compromise between a point of complete vertical mixing of the effluent while limiting the distance over which decay could not be modelled.

A diffusion factor uh^2E_z, for the region around the discharge is required as input for the analytical solution. An approximate value for the diffusion factor uh^2E_z of 0.010 m^2/s was calculated based upon estimates of local streamflow characteristics and estimated transverse mixing coefficients.

The first cross section at which the plume occupied enough of the flow area to allow for an accurate assessment of the upstream mixing behaviour was at cross section 3. The flow area occupied by the plume at cross section 1 was less than 1.5% of the total flow. Similarly, at cross section 2, less than 3% of the discharge was occupied by the plume.

The mixing coefficients at cross sections 1 and 2 were assumed equal, and were adjusted to obtain the best fit to the dye data at cross section 3.

TRSMIX does not take a transverse mixing coefficient as direct input, but instead requires a dimensionless mixing coefficient (β), a length scale (l), and the mean channel shear velocity (u_*). E_z is then calculated as

$$E_z = \beta \, l \, u_* \tag{6.2}$$

There is currently contention in the literature as to the most appropriate length scale (l) to represent turbulence scales in natural streams. Turbulence is often scaled upon using either a width scale such as channel width (Lau and Krishnappen, 1981) or a depth scale, such as the hydraulic radius (Beltaos, 1980; Krishnappen and Lau, 1982). However, these are both usually scaled upon mean-channel properties, and may not be representative of conditions along the banks of a wide stream. Gerard et al. (1985) reported the half-plume width $\bar{b}$ to be the most appropriate scale for near-bank mixing. As mentioned, the half-plume width $\bar{b}$ is defined as the transverse distance across the plume from c'_{max} to $0.5c'_{max}$. In this study, the half-plume width was selected as the most appropriate length-scale for use in Equation 6.2. It was measured from plots of concentration vs. transverse distance obtained from the dye test.

Under certain input and modelling conditions, oscillations developed in the numerical solution. These probably resulted from numerical dispersion and rounding errors, and are often a result of inappropriate transverse and longitudinal grid spacing in the finite difference steps. A course longitudinal grid spacing combined with large concentration gradients often causes the greatest oscillations (Putz, 1983; Krishnappen and Lau, 1982).

Krishnappen and Lau (1982) recommended that the longitudinal grid spacing be set using the following criteria:

$$\frac{(uh^2E_z)\,\Delta x}{Q^2\,(\Delta\eta)^2} \equiv 1 \tag{6.3}$$

Putz (1983) found that the boundary regions were the most instrumental in creating the oscillations, and suggested that local values for uh^2E_z within this region be used in computing the grid spacing. Using the above criteria for the Rossdale mixing data did not provide acceptable results, and unacceptable oscillations still developed in the solution.These oscillations were reduced by reducing the transverse grid spacing to η=0.01, and by use of the mean channel properties for computation of the longitudinal grid spacing in equation 6.3. The only exception to this was for the region immediately downstream from the discharge, where a grid spacing of 1.0 m appeared to give the most stable solution.

The transverse mixing coefficient E_z was determined downstream of each successive cross section by matching predicted distributions to observed profiles. The transverse mixing coefficient which provided the closest approximation to the observed data was then selected. Selected values for E_z and β downstream from each cross section are reported in Table 6.2. Figures 6.4a to 6.4d show a comparison of predicted and observed results for cross sections 3 to 6.

6.1.2 Residual Chlorine Surveys

Field investigations of the distribution of residual chlorine were conducted downstream from Rossdale's Plant 3 outfall. A discharge flowrate of 32.5 ML/d was obtained out of the Plant 3 outfall, with a mean chlorine residual of 2.12 mg/L. The mean discharge in the North Saskatchewan over the monitoring period was 196.0 m^3/s. Residual chlorine concentration profiles were determined at cross sections 1,2,3, and 4. An additional cross section, 1A, was also sampled to provide additional data on the plume.

Chlorine residuals in Rossdale's discharge waters typically vary between 1.85 to 2.05 mg/L as Cl_2. This residual is composed of chloramines, with no detectable free chlorine observed. The mean residual over the test period was 2.12 mg/L, with observed residuals varying between a low of 2.05 mg/L and a high of 2.16 mg/L. An analysis of relevant parameters of the treated water is provided in Table 6.3.

Results from the analysis of downstream chlorine concentrations are presented in Figure 6.5. Raw field data from the chlorine plume is provided in Appendix E, along with summary statistics. Figure 6.6 presents the data in dimensionless form.

As expected, the total residual chlorine concentrations in the plume decreased quite rapidly. The furthest downstream cross section at which any detectable chlorine residual was present was cross section 3, approximately 1400 m downstream from the discharge point. Measurements were attempted at cross section 4, but no residual greater than the detection limit of 0.01 mg/L was observed. Inspection of Figure 6.5 indicates that the plume maintained very close contact with the north bank. Detectable chlorine residuals at

Table 6.2. Transverse mixing coefficients β and E_z.

Cross section	β	E_z (m^2/s)
1	0.06	0.0156
2	0.06	0.0403
3	0.61	0.284
4	0.44	0.462
5	0.16	0.893

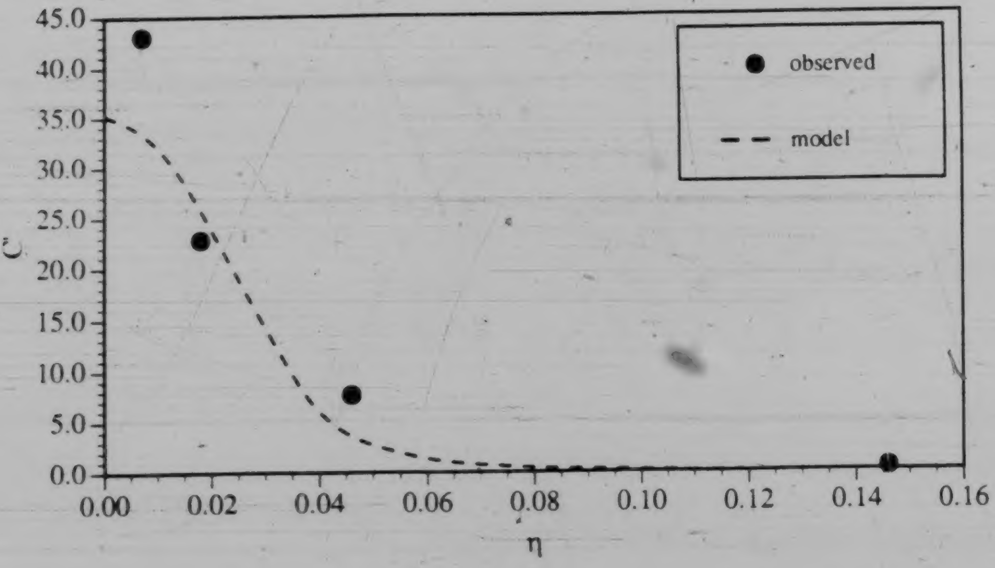


Figure 6.4a Model fit vs. observed tracer distribution: Rossdale cross section 3.

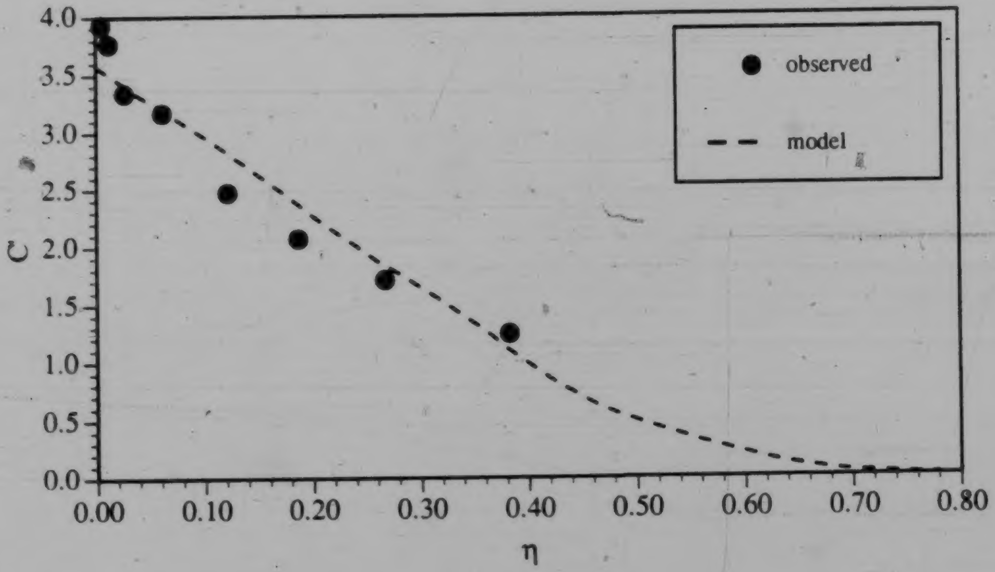


Figure 6.4b Model fit vs. observed tracer distribution: Rossdale cross section 4.

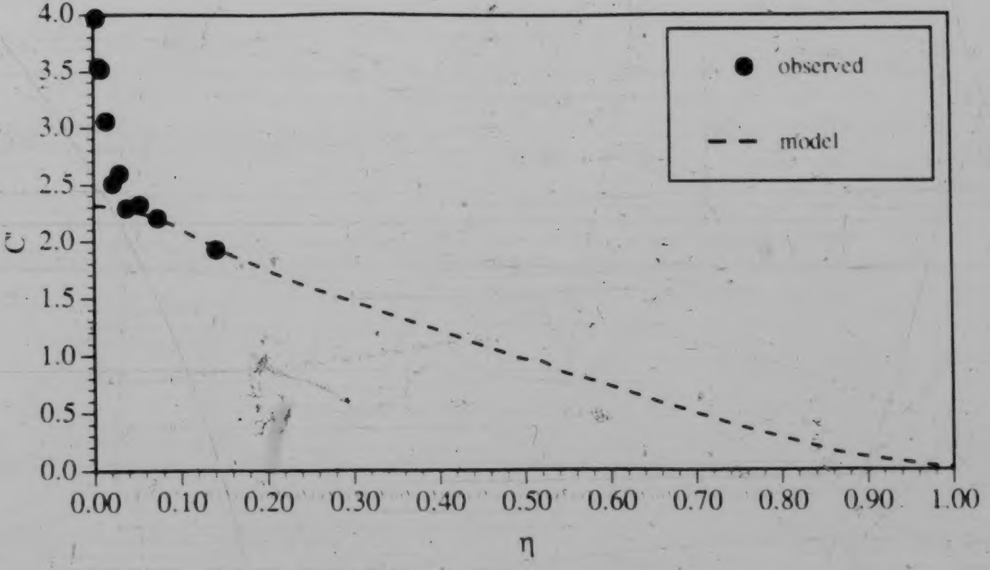


Figure 6.4c Model fit vs. observed tracer distribution: Rossdale cross section 5.

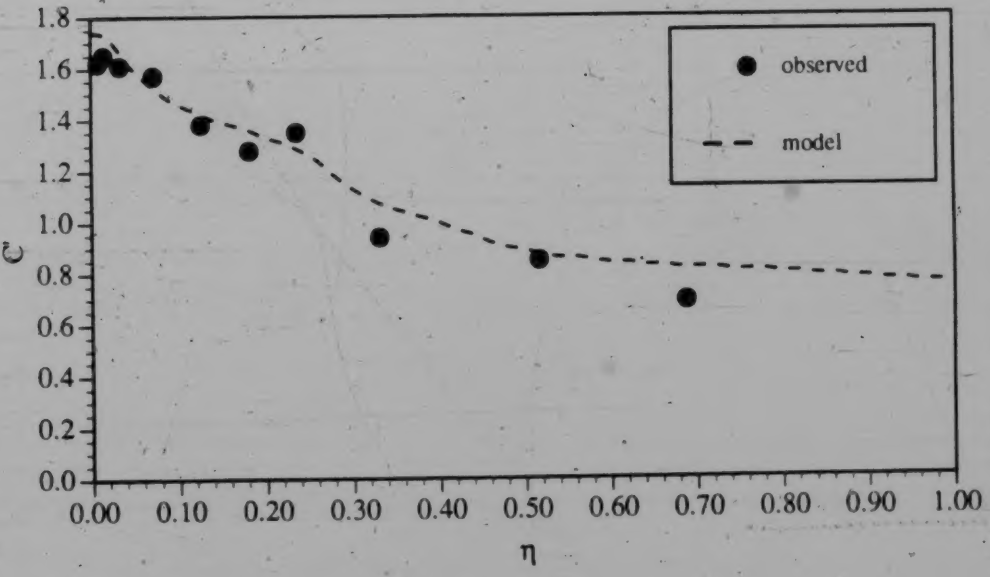


Figure 6.4d Model fit vs. observed tracer distribution: Rossdale cross section 6.

Table 6.3. Analysis of Rossdale Plant 3 Water Quality Parameters (September 6, 1990).

Parameter	Value
pH	8.3
Temperature (°C)	17
Turbidity (NTU)	0.05
total hardness (mg/L) as $CaCO_3$	163
calcium hardness (mg/L) as $CaCO_3$	115
alkalinity (mg/L)	112
U.V. absorbance (@ 200 nm)	5.5
TTHM (mg/L)	0.003
volatile organic carbon (mg/L)	0.001
total oxidants (mg/L)	0.36

Source: City of Edmonton (1990)

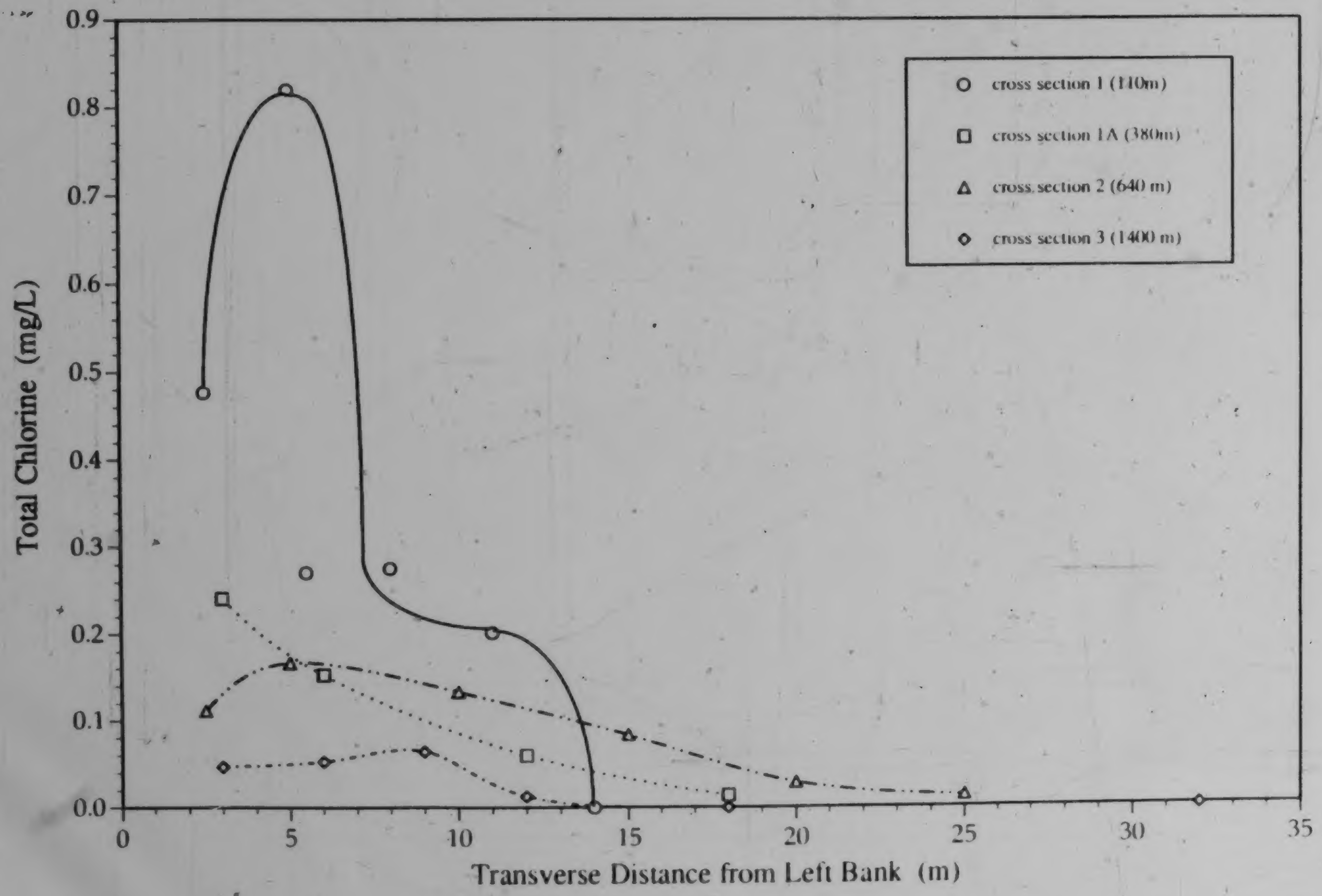


Figure 6.5 Residual chlorine profiles: Rossdale cross sections 1 to 3.

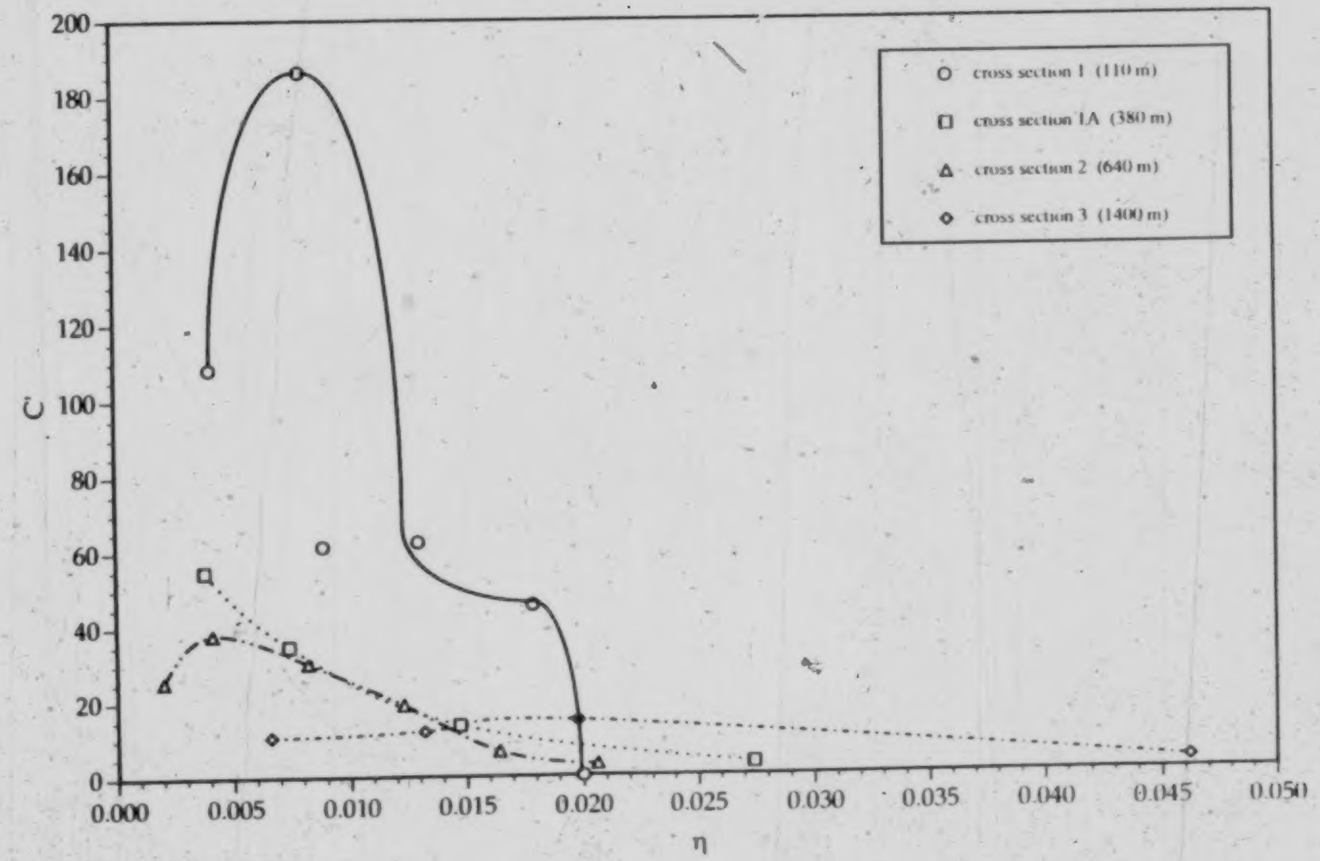


Figure 6.6 Dimensionless chlorine profiles: Rossdale cross sections 1 to 3.

downstream cross sections were observed only within the first 5% of the total flow (η=0.05).

6.1.2.1 Chlorine Mass Balance Analysis

A mass balance on the total residual chlorine flux at each cross section was made to obtain an initial approximation of in-stream chlorine decay rates. The total mass at each cross section was calculated using the chlorine residual profile and observed velocity data. Estimates of the mass at each cross section should be reasonably accurate, as the plume was quite well defined over its transverse dimension, and as it was followed until concentrations dropped below the detection limit. Similar to the error sources discussed in the tracer mass balance, some error in the mass estimates may also have resulted from errors in the channel geometry and streamflow property values.

The log of mass (or flux) was plotted against the calculated residence time in the river. For the purposes of the mass balance, the assumption that the transport time from the outfall to any cross section was constant across the total width of the plume at that cross section was made. This does not accurately simulate the physical conditions, as velocities along the bank would naturally be lower due to to effects of the bank shear. This assumption will have the effect of slightly over-estimating the decay rate coefficient. The transport time was calculated based upon the mean of local velocities across the plume, and results are plotted in Figure 6.7.

A first-order decay expression provided a good fit to the observed data, and yields values for k of 41 d^{-1} and 59 d^{-1} respectively for the plume-averaged and η = 0.02 velocity conditions. It would be expected that the plume-averaged velocity predictions would provide a more accurate description of the streamflow behaviour, and greater confidence should be placed in this prediction. Although the above analysis is limited due to the inherent assumptions, it does provide a valuable estimation of the decay rate coefficient.

6.1.2.2 Decay Coefficient Determination

Following analysis of the tracer data, the mixing behaviour of the plume was reasonably well described, and a datum from which to assess chlorine decay rates existed. Any differences between the observed chlorine concentration and that predicted through the mixing analysis could be attributed to chlorine decay within the stream. As discussed, these losses can result from reactions with chemical constituents in the river water matrix,

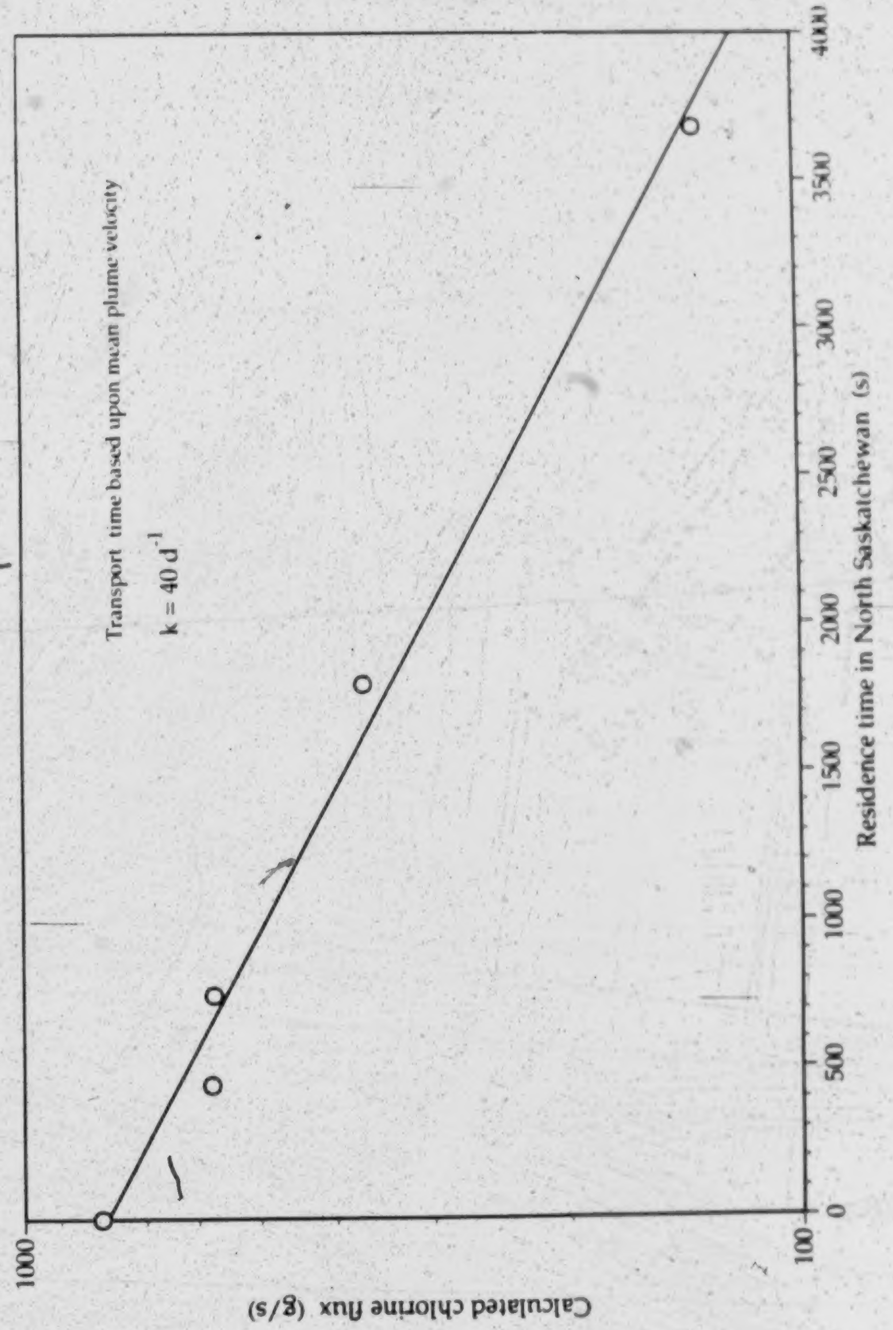


Figure 6.7 Chlorine flux vs. residence time (based on mean plume velocity).

photochemical decay, volatilization, benthic demand, and adsorption to sediments. As the chlorinated water discharges were neutrally bouyant, they should mix in the same manner as the tracer. The chlorine plume was discharged from the outfall with a small transverse velocity, but this velocity is probably insignificant, and would not be expected to alter the initial mixing behaviour from that seen with the dye plume. From visual inspection, the centre of the chlorine plume was approximately in-line with the tracer discharge.

Several runs were made with TRSMIX, altering the value of the decay coefficient k until a best fit to the observed data was obtained. The chlorine decay coefficient was assumed constant throughout the study reach. This should be a valid assumption, as the decay coefficient is primarily a function of the chemical and mean turbulence properties of the stream, and significant changes in these parameters over the short reach of interest would not be expected.

Similarly to the difficulties observed in the tracer study, cross section 3 was the nearest point to the discharge at which it was possible to model the in-stream chlorine distribution. Figure 6.8 shows the chlorine profiles for various values of k at cross section 3 as predicted by TRSMIX. Where available, the mean of the triplicate samples is also plotted along with the 90% confidence intervals. A 90% level of significance was selected due to the low degrees of freedom associated with the few replicate samples available. The 90% confidence intervals are quite large for two of the data points, extending over an approximate range of ± 8 c'. This corresponds to an actual concentration range of ± 0.03 mg/L. The observed variance on the samples may be attributed to the turbulent nature of the stream and to the nearby proximity of the bank where local eddies with differing concentrations of chlorine may exist .

Due to the scatter observed in the chlorine data, and the wide confidence limits on two of the samples, it is somewhat difficult to select the most appropriate value for k. A decay rate coefficient of 26.0 d^{-1} appears to provide the best fit to the data, but underestimates the concentration observed at $\eta = 0.02$. Conversely, $k=10.0\ d^{-1}$ appears to provide a reasonable lower bound on the decay coefficient as all of the observed data points are bounded by this value.

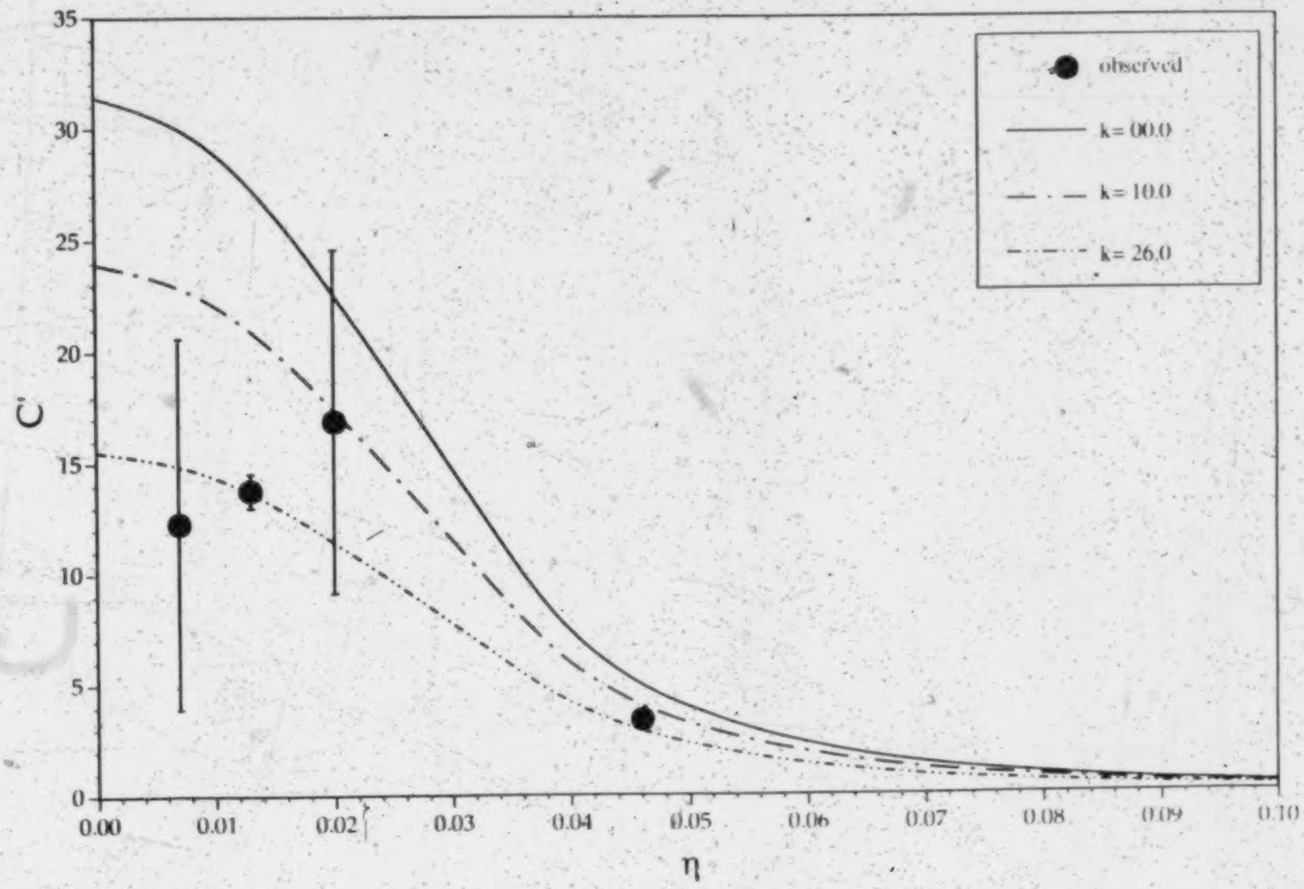


Figure 6.8 Model predictions of TRC distribution at Rossdale cross section 3 for various decay coefficients.

6.1.3 Microbiological Study

A series of microbiological samples were collected at the same time as the chlorine plume was sampled. The objective was to determine in a qualitative manner the effect of residual chlorine on the in-stream bacterial population, and to determine whether the chlorine plume produced a noticeable effect on the in-stream microbial population over the short contact times encountered. The standard indicator organisms of total heterotrophs, total coliforms, and fecal coliforms were enumerated. Anderson et al. (1986) and Coleman et al. (1974) provide a more detailed description of microorganism distribution and speciation along the North Saskatchewan River through Edmonton.

Microbial distributions within the chlorine plume are summarized in Figures 6.9a to 6.9c for total heterotrophs, total coliforms and fecal coliforms respectively. Collected data is also provided in Appendix F. A general trend towards reduced populations along the bank was observed. It would be expected that an opposite trend to that observed with the dye and chlorine tests would be observed with microbial samples. That is, a reduced population should be seen along the bank, where chlorine concentrations are highest. Further downstream, the concentration difference would not be as great, but the effects would be seen further into the main flow. This collected data were generally seen to behave in this manner.

Anderson et al. (1986) reported near-bank total and fecal coliform counts at the Rossdale Water Treatment Plant were significantly higher than those obtained from centre-channel samples. These elevated populations were attributed to inputs from along-bank sewer discharges. The reduction in total counts seen along the bank suggests that the effects of the chlorine residual was felt by the microbial population. No attempt to separate the bactericidal effects of the chlorine residual from the simple dilution of the river water with treated discharge water was made.

Several storm and combined sewers exist along the north bank between the outfall and cross section 3. Inputs from these sources were not quantified for this study, but probably resulted in significant contributions to the in-stream microbial population. Due to the limited data, and with no quantification of additional sources along the study reach, interpretation of the data is difficult.

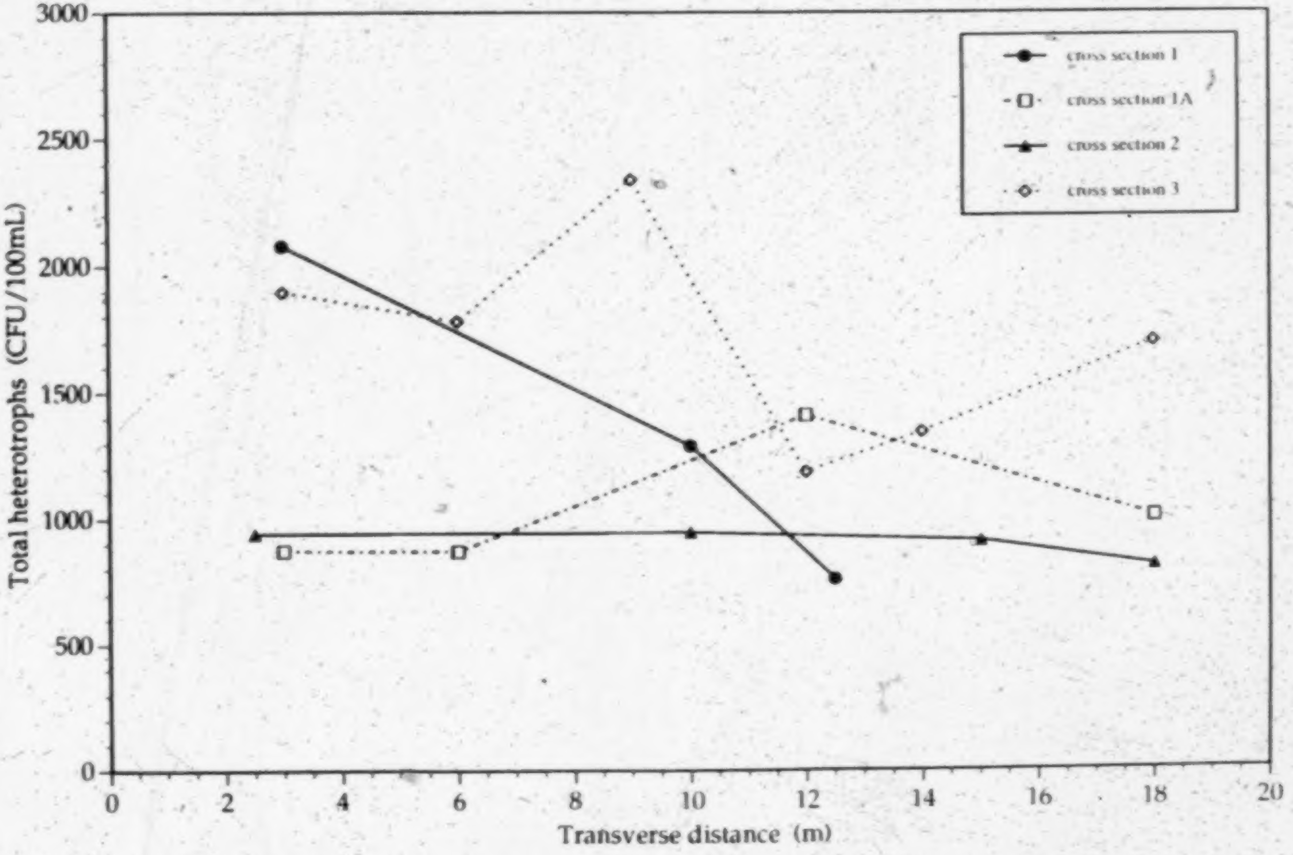


Figure 6.9a Total heterotroph distribution in the Rossdale chlorine plume.

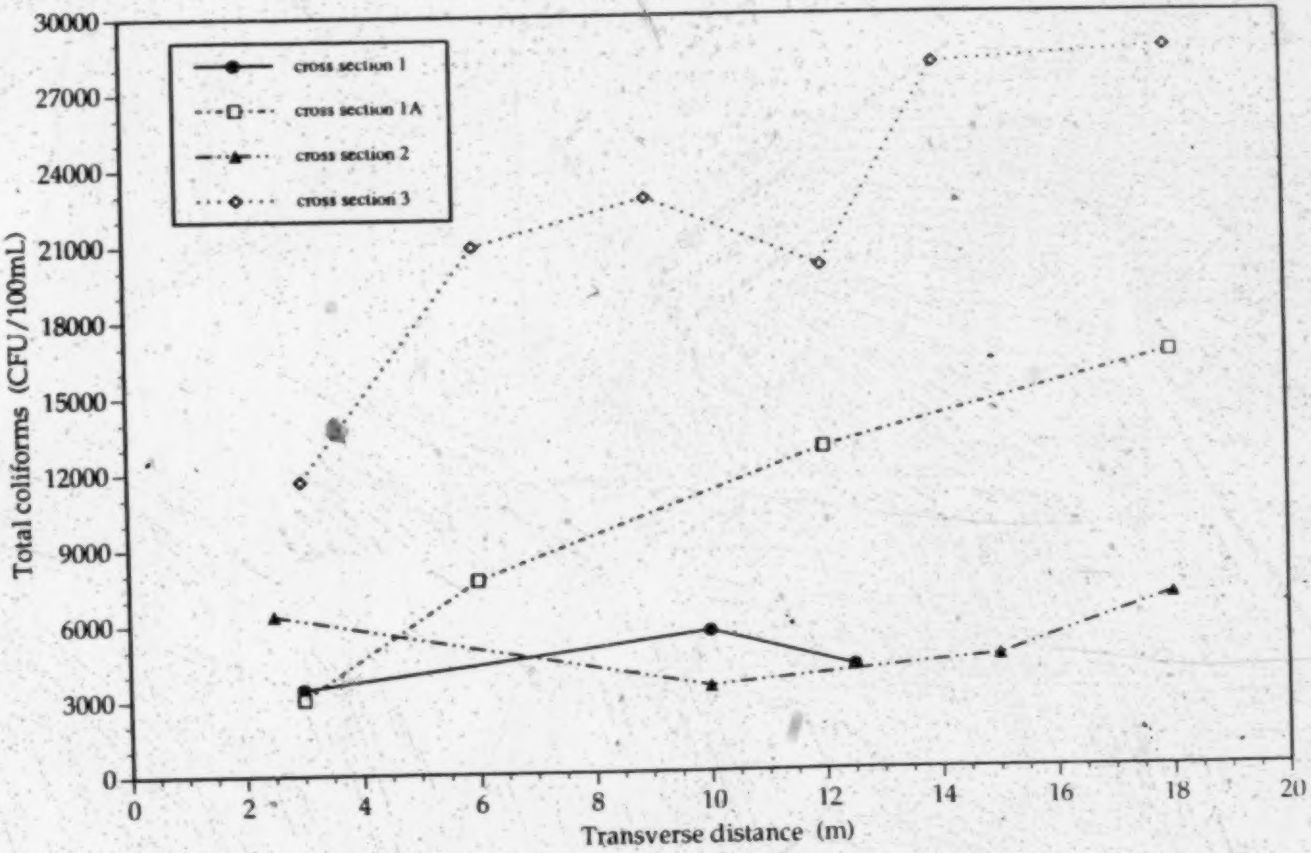


Figure 6.9b Total coliform distribution in the Rossdale chlorine plume.

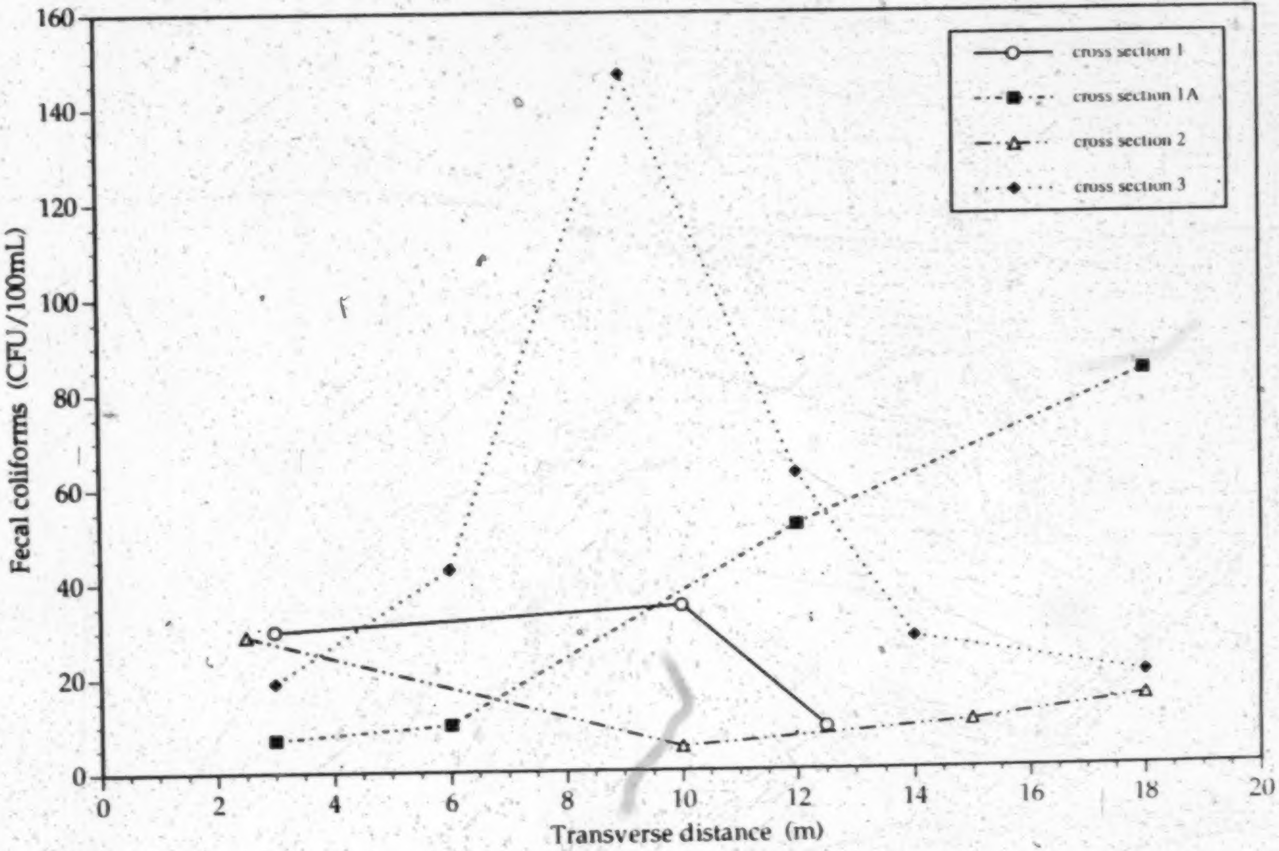


Figure 6.9c Fecal coliform distribution in the Rossdale chlorine plume.

6.2 E.L. Smith Water Treatment Plant Field Study

Results from the field investigations at the E.L. Smith Water Treatment Plant are presented below. The dye test was conducted on September 26, 1990, with the chlorine plume test following the next day. The mean discharge in the North Saskatchewan over the study period was 145.6 m^3/s during the tracer study, and 146.8 m^3/s during the chlorine study. The E.L. Smith study paralleled previous work conducted at Rossdale, but was conducted to obtain data specific to conditions at E.L. Smith. Sampling of the chlorine plume was extended to include a night sampling program from which the effects of UV light on in-stream chlorine persistence could be determined.

6.2.1 Rhodamine WT Tracer Test

Results from the Rhodamine tracer study are plotted in Figures 6.10a to 6.10c. These provide observed tracer profiles at each of the established cross-sections. Plots of dimensionless tracer concentration c' vs. dimensionless transverse distance η are provided in Figures 6.11a to 6.11c, and the raw tracer data is summarized in Appendix C.

During the tracer study, visible traces of the dye were observed as far downstream as cross section 2, 465 m downstream. Due to the variable hydrography along the bank between cross sections 1 and 2, the plume did not follow a straight path, and significant lateral movement was observed, indicating the existence of significant transverse velocities along this area. Several large stationary eddies and 'pools' were present along the riverbank, but no visible accumulation of dye was observed over the study period.

Statistically, the same general behaviour was observed in replicate samples collected during this study as was observed during the Rossdale study. The largest variation in replicate analyses was observed at the upstream cross sections, and along the outside edge of the plume. The variations along the edge of the plume would be expected, as this is where the plume is mixed with the main flow. Within the main body of the plume, the coefficient of variation between replicates was usually less than 10%, and often less than 5%. These values are well within the range normally observed in field situations.

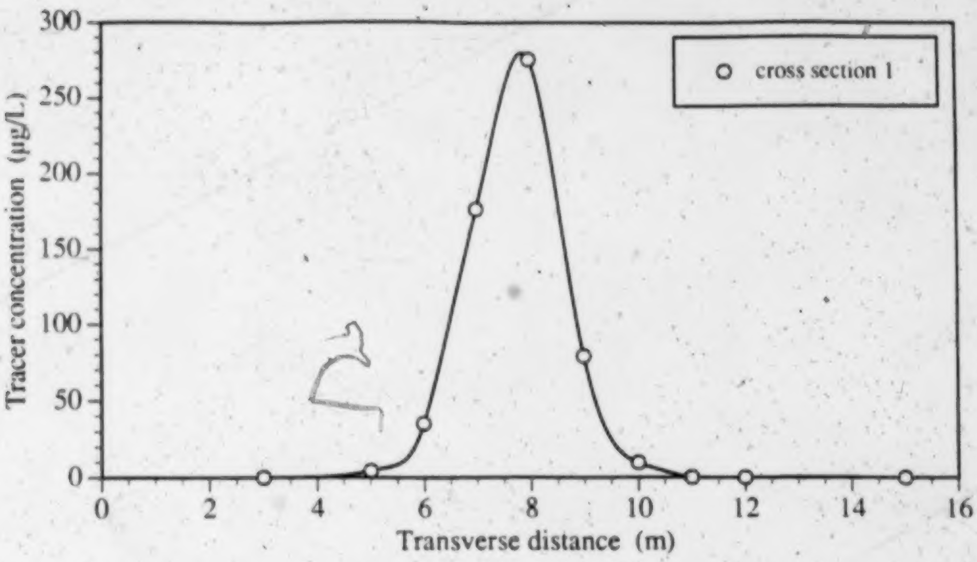


Figure 6.10a Rhodamine WT tracer profile: E.L. Smith cross section 1.

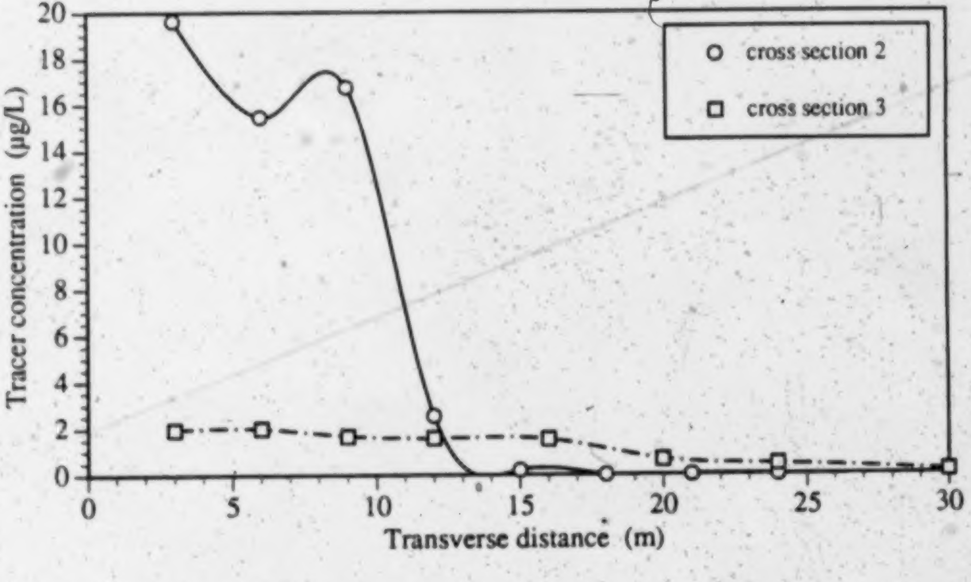


Figure 6.10b Rhodamine WT tracer profile: E.L. Smith cross sections 2 and 3.

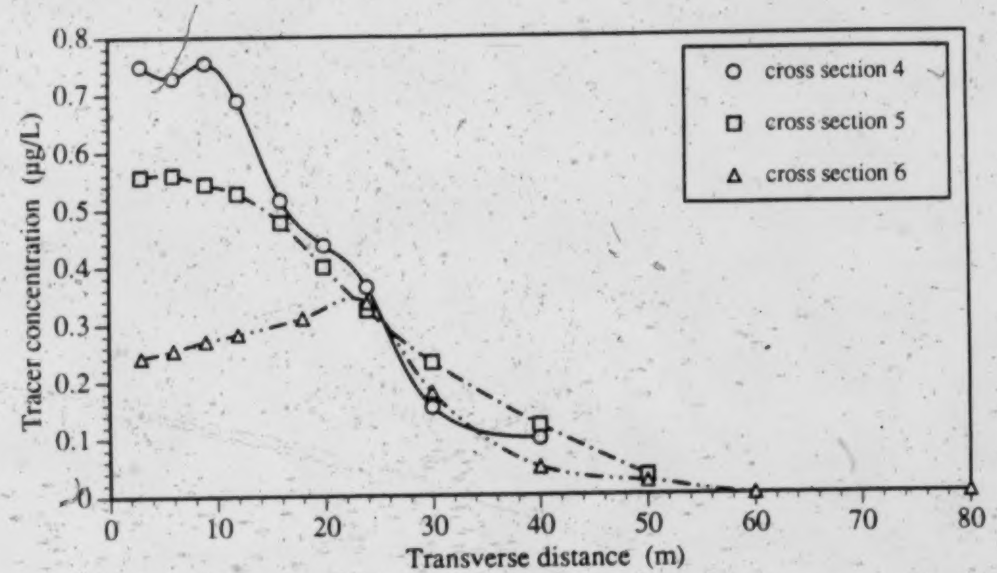


Figure 6.10c Rhodamine WT tracer profile: E.L. Smith cross sections 4 to 6.

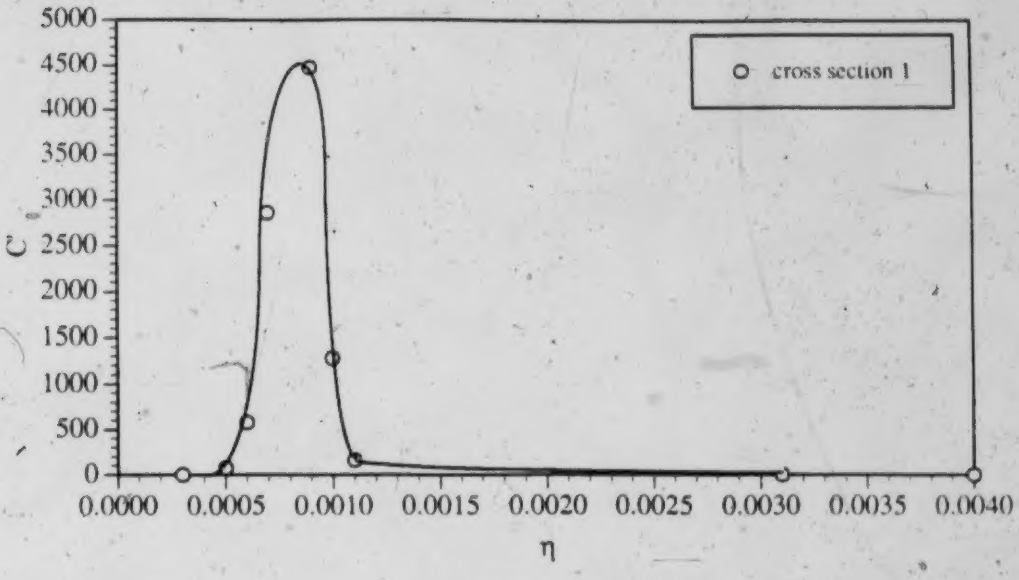


Figure 6.11a Dimensionless tracer profile: E.L. Smith cross section 1.

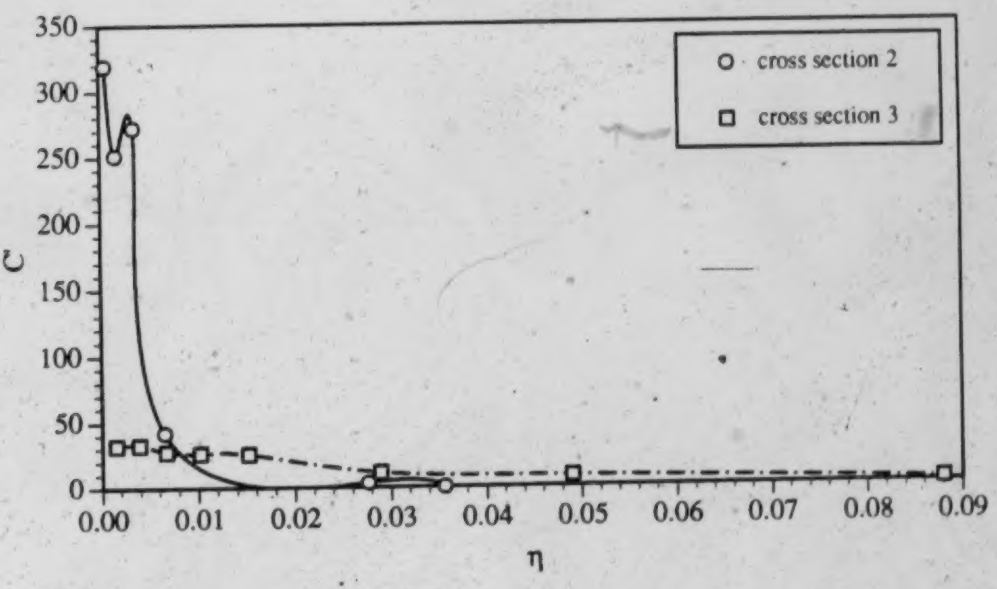


Figure 6.11b Dimensionless tracer profiles: E.L. Smith cross sections 2 and 3.

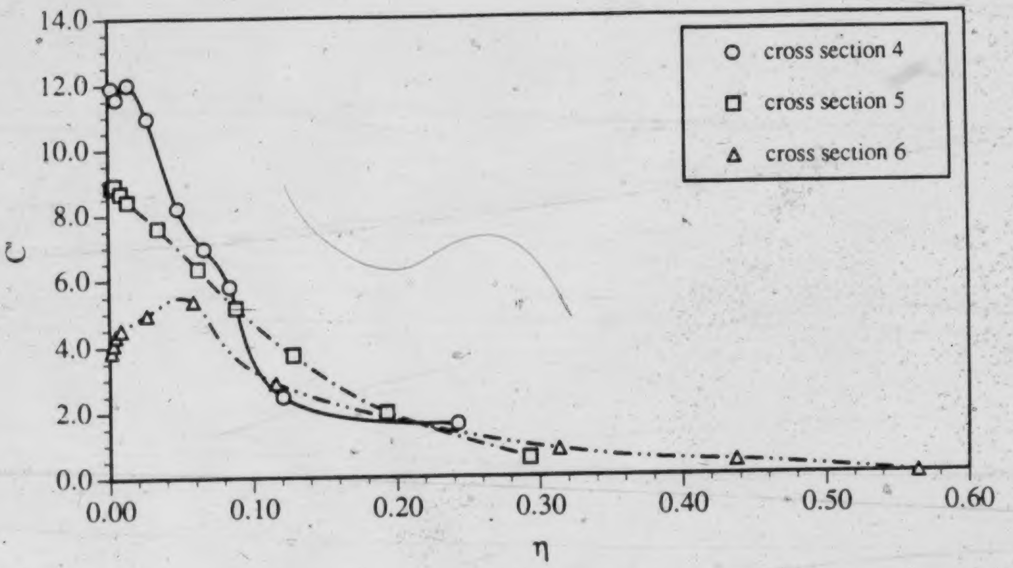


Figure 6.11c Dimensionless tracer profiles: E.L. Smith cross sections 4 to 6.

6.2.1.1 Mass Balance Analysis

A mass balance on the tracer flux at downstream cross sections was conducted using local velocity predictions generated by the program TRSMIX.DV, along with local cross-sectional geometry and tracer concentration data. As described, TRSMIX.DV proportions the total flow across the channel into streamtubes using the surveyed cross-sectional geometry and the Manning resistance equation. Calculation of the mass balance using the synthesized velocity data indicated very inconsistent recoveries, as can be seen in Table 6.4. Calculated mass recoveries from 58% to 550% of the predicted traced mass were observed over the relatively short distances involved.

Similar to the situation at Rossdale, very little change in total tracer mass would be expected in the short distances and travel times involved in this study. There was a high degree of confidence in the injected tracer flux value, upon which the percentage recoveries were calculated. The tracer was injected through a previously calibrated peristaltic pump, which showed no detectable flowrate change over the period of the study. The injected tracer concentrations were also reliable, as samples of the stock solution were obtained, and no obvious variation found. The data required for the mass balance calculations includes the transverse variations in tracer concentration, current velocity, and ~~cross~~ sectional geometry at each cross section. From consideration of data used to calculate the mass balance, two plausible sources of error were identified.

At cross sections 1 and 2, the plume width was very narrow. The total plume width at cross section 1 was 6 m, with 7 samples collected. At cross section 2, Rhodamine WT was only detected in 5 samples over a 12 m width. Tracer concentration gradients were very high, and as a linear relationship in concentration between adjacent sample points was assumed, the accuracy of the mass balance integration is poor. The calculation is extremely sensitive to an error or anomaly in one value. The high sensitivity of the calculation and the uncertainty in parameter estimation suggests that the calculated recoveries could be highly variable.

A second error source in the mass balance calculation may explain the variations observed further downstream, where the geometry and plume were both more well defined. Results from the previous investigation at Rossdale indicated that the TRSMIX.DV predictions were not providing good velocity estimates along the near-bank zone. In the mass flux calculation, the flux across any cross-section is directly related to the local velocities at that

Table 6.4. Rhodamine WT tracer mass balance.

Cross section	initial tracer flux (mg/s)	initial tracer recovery (%)
1	14.60	151
2	53.49	553
3	19.50	202
4	11.71	121
5	11.21	116
6	5.60	58

section and an error in velocity measurements will translate directly into an error in the mass flux through the integral. As the ability of TRSMIX.DV to predict local velocities along the streambank has been shown to be poor, over-estimations of the local velocities at these sections may explain the inability to obtain 100% tracer recoveries.

The implausible results observed in the mass balance calculations were attributed to inaccuracy in the velocity estimates used in the flux calculations for cross sections 3 to 6. Unfortunately, no field velocity measurements were obtained at E.L. Smith to confirm this assumption. However, this assumption should be reasonable, as the tracer data indicated a low coefficient of variation among the replicate samples, and as the channel cross-sectional data was considered accurate.

As the calculated recoveries varied from 58 to 200% of the predicted flux, this would suggest that the velocity estimates were in error by as much as a factor of two. Errors in the synthesized local velocities of this magnitude could be expected due to the severity of the river bend as it flows around Terwillegar Park and from the highly variable flow profiles observed near the bank. Strong secondary currents may also have existed, causing the actual velocity profile to differ substantially from that predicted. The synthesized local velocities along the left bank were therefore adjusted to yield a 100% mass recovery. The adjusted velocities probably provide a more representative description of the actual hydraulic conditions over this complicated length of river. The cumulative flow profiles were recalculated to conform to the adjusted conditions, and the overall change to the total flow caused by adjusting the near-bank velocity field was essentially negligible.

6.2.1.2 Transverse Mixing Coefficient Determination

Transverse mixing coefficients downstream from E.L. Smith were obtained using the same iterative procedure employed in the Rossdale data analysis. The initial dye distribution was generated using an analytical solution to 60 m. To reduce oscillations and numerical dispersion, the transverse grid spacing was reduced to $\eta = 0.005$. Upstream of cross section 3, the flow area occupied by the plume was too small to provide adequate plume resolution for determination of the mixing coefficients. The dimensionless mixing coefficient β which provided the most accurate simulation of the tracer distribution at cross section 3 was selected and assumed constant for cross sections 1 and 2.

Results from the tracer distribution modelling are presented in Figures 6.12a to 6.12d. The results of the modelling are summarized in Table 6.5.

6.2.2 Residual Chlorine Surveys

Field investigations of the distribution of residual chlorine downstream from E.L. Smiths bank outfall were conducted on September 27, 1990. Residual chlorine concentration profiles were determined at cross sections 1,2,3, and 4. The mean total chlorine residual over the test period at E.L. Smith was 2.06 mg/L, with a maximum of 2.10 mg/L and a minimum of 2.04 mg/L observed. This residual was composed of chloramines, with no detectable free chlorine present. An analysis of relevant parameters of the treated water is provided in Table 6.6.

At the time of the chlorine plume test, the raw water flowmeter at the plant was out of order, making an exact metering of the discharge flowrate impossible. An estimation of the discharge flowrate was made by examination of chemical consumption data, an in-plant water balance, and estimation of standard operating losses. From the above data, the best estimate of the discharge flowrate over the period of the chlorine plume test was 32.5 ML/d with an expected accuracy of ±10%.

6.2.2.1 Chlorine Survey Results

Based on results from the day-time in-field enumeration of total residual chlorine downstream from E.L. Smith, the cross-sectional TRC profiles in Figure 6.13 were developed. The data is presented in dimensionless form in Figure 6.14. Raw data from both the day-time and night sampling is summarized in Appendix E. Inspection of Figure 6.13 indicates that total residual chlorine concentrations in the plume decreased quite rapidly. At cross section 4, 1750 m downstream from the discharge, residuals were very near the detection limit, and no detectable chlorine was observed at cross section 5, 2445 m downstream.

6.2.2.2 Decay Coefficient Determination

The in-stream chlorine decay rate was determined by solving Equation 2.19 numerically, and comparing the predicted chlorine distribution at cross section 3 to the field data. Although residual chlorine was detected at cross section 4, it was impossible to use this additional field data as the numerical solution was not able to adequately model the mixing

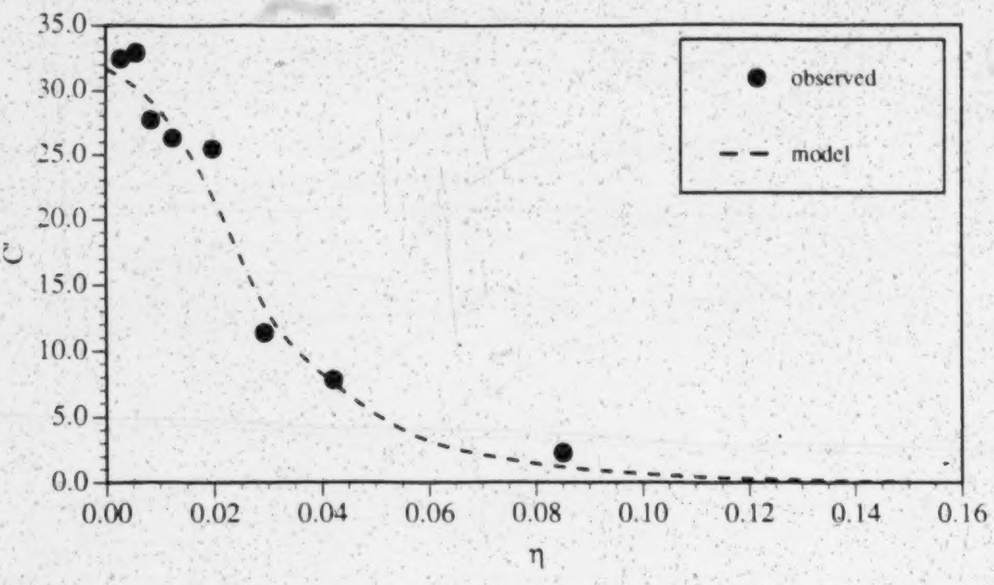


Figure 6.12a Predicted vs. observed tracer distribution: E.L. Smith cross section 3.

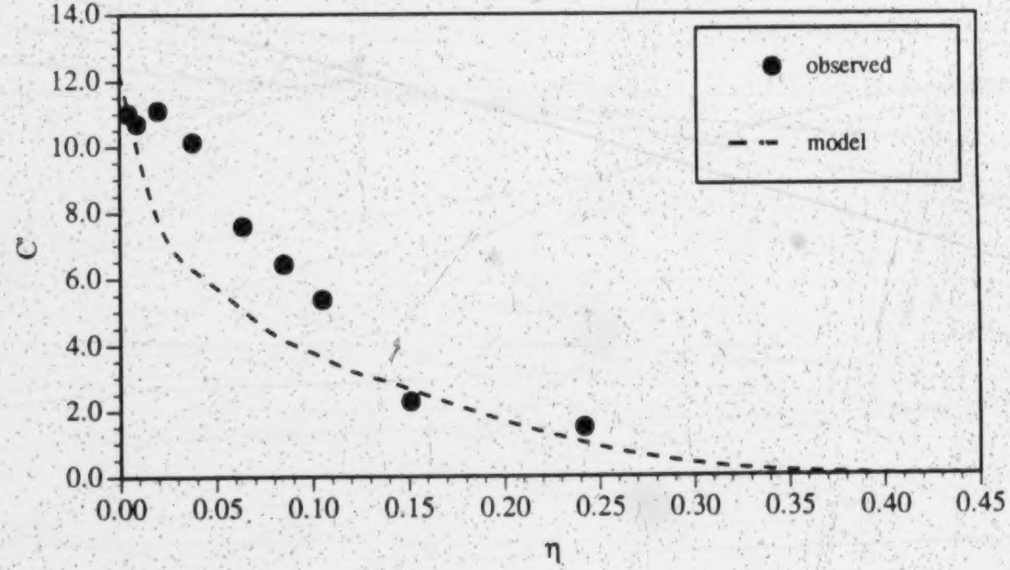


Figure 6.12b Predicted vs. observed tracer distribution: E.L. Smith cross section 4.

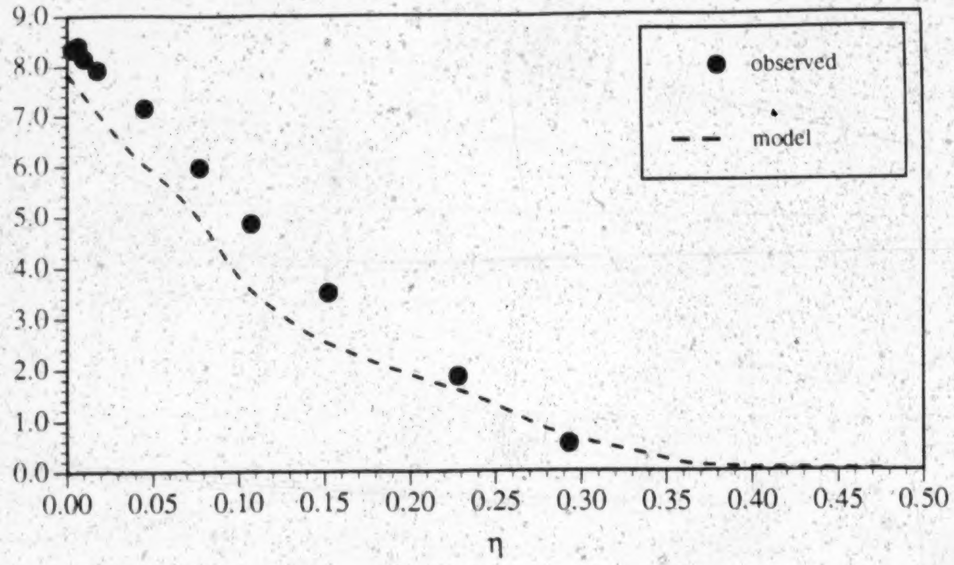


Figure 6.12c Predicted vs. observed tracer distribution: E.L. Smith cross section 5.

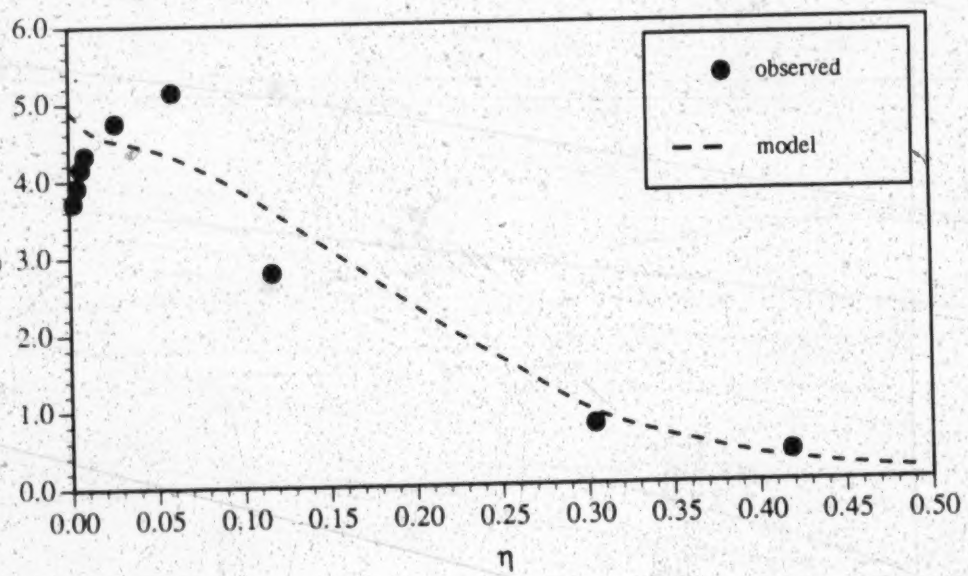


Figure 6.12d Predicted vs. observed tracer distribution: E.L. Smith cross section 6.

Table 6.5. Transverse mixing coefficients β and E_z.

Cross section	β	E_z (m^2/s)
1	0.21	0.0173
2	0.21	0.0328
3	0.08	0.0847
4	0.05	0.0507
5	0.08	0.0800

Table 6.6. Analysis of E.L. Smith treated water water quality parameters (September 26, 1990).

Parameter	Value
pH	8.3
Temperature (°C)	14
Turbidity (NTU)	0.03
total hardness (mg/L) as Ca CO_3	110
calcium hardness (mg/L) as Ca CO_3	64
alkalinity (mg/L)	68
U.V. absorbance (@ 200 nm)	2.8
TTHM (mg/L)	0.001
volatile organic carbon (mg/L)	< 0.001
total oxidants (mg/L)	0.24

Source: City of Edmonton (1990)

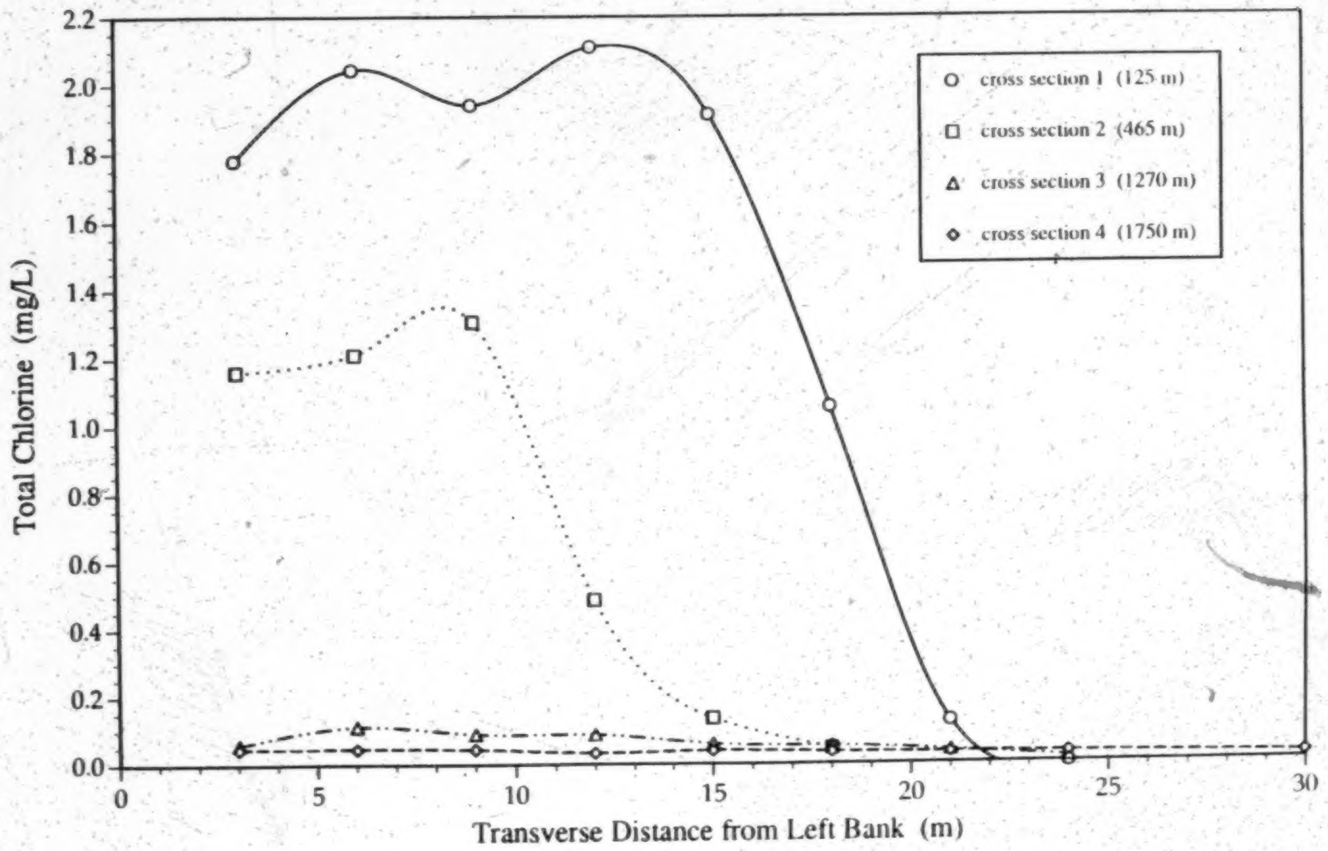


Figure 6.13 Residual chlorine profiles: E.L. Smith cross sections 1 to 4.

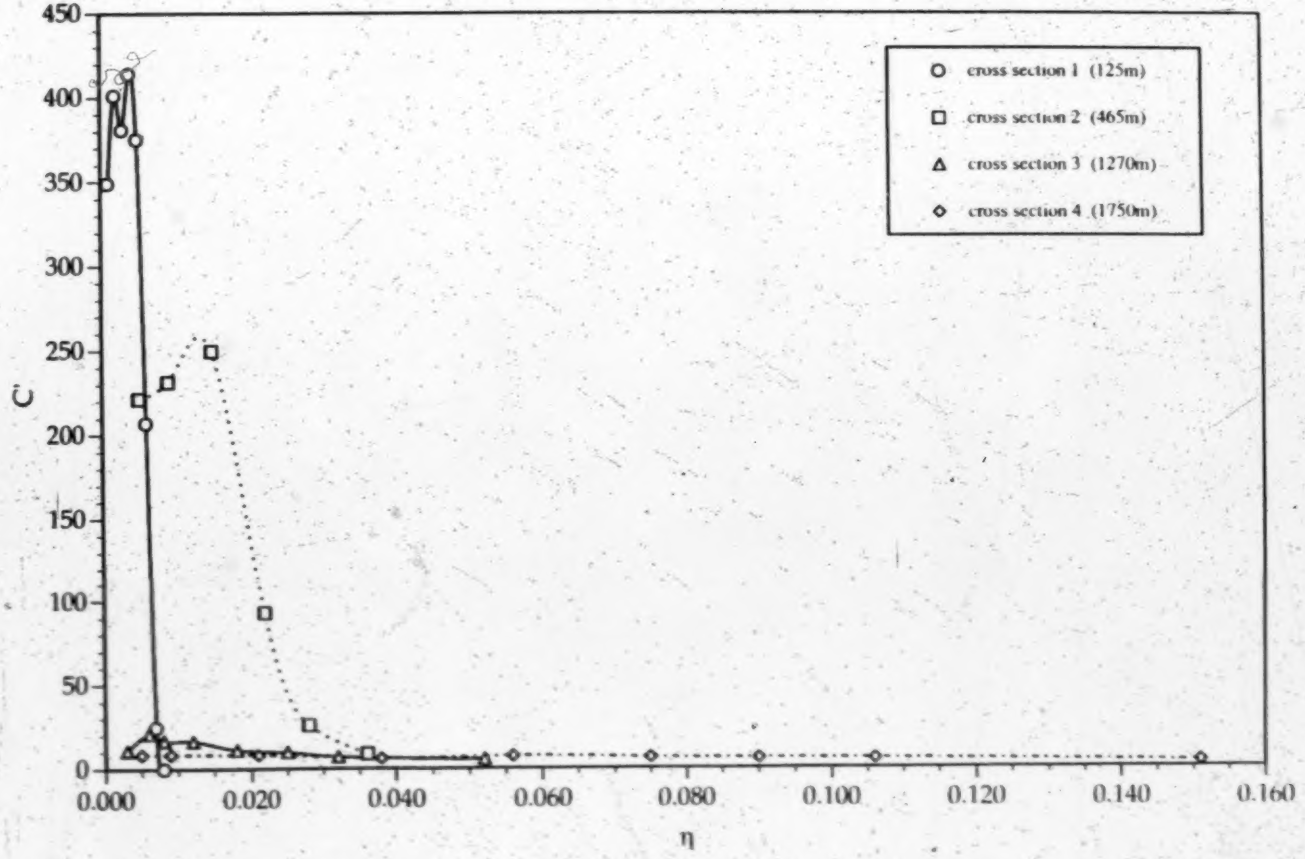


Figure 6.14 Dimensionless chlorine profiles: E.L. Smith cross sections 1 to 4.

process within this section of the river. Very good agreement between the tracer and predicted profiles were observed at cross section 3. This suggests that the upstream mixing behaviour was well described, and the following discussion therefore focuses on analysis of the data available for this cross section.

The numerical prediction of the tracer concentration profile at cross section 3 was used as the datum for determination of the first-order decay coefficient. The observed chlorine distribution, along with the conservative solution and the numerical solution for various decay coefficient values are plotted in Figure 6.15. Only the mean value of replicate chlorine samples is reported for each transverse location. Some scatter of the field data is expected due to the inherent variability of the sampling and mixing processes, and the 95% confidence intervals for the observed data are plotted to aid in interpretation of the results. The wide range of several of the confidence limits results from the low number of replicate samples, and the correspondingly few degrees of freedom available.

The first data point, at $\eta = 0.003$, was excluded from consideration due to its proximity to the riverbank. Two samples were collected at this point, with the concentration being well below values farther away from the bank. These samples may have been trapped along the bank in a pool which would have provided a longer residence time and consequently, a greater decay, or the lower concentrations may be due to the location of the effluent discharge, the centre of which was about 8 m from the bank. Insepection of Figure 6.13 indicates that at all cross sections, reduced concentrations were found immediately adjacent to the bank, and consideration of the physical problem suggested that this point was erroneous.

Samples collected along the outer edge of the plume, at $\eta = 0.052$ were analyzed, with only one of the two samples obtained containing chlorine at concentrations greater than the detection limit. The variability seen at this point is a consequence of the mixing of eddies of varying chlorine concentration along the outer fringes of the plume. Although no chlorine was detected in the second sample, it may well have been present, but at a concentration below the level of quantitation. This was considered to be an important observation, and to adequately represent the time-averaged physical characteristics of the plume, this data point was kept. A concentration value equal to the limit of detection was assigned to the second sample to enable calculation of a mean concentration at that location. Although this simple substitution method of estimation is not based on any rigourous

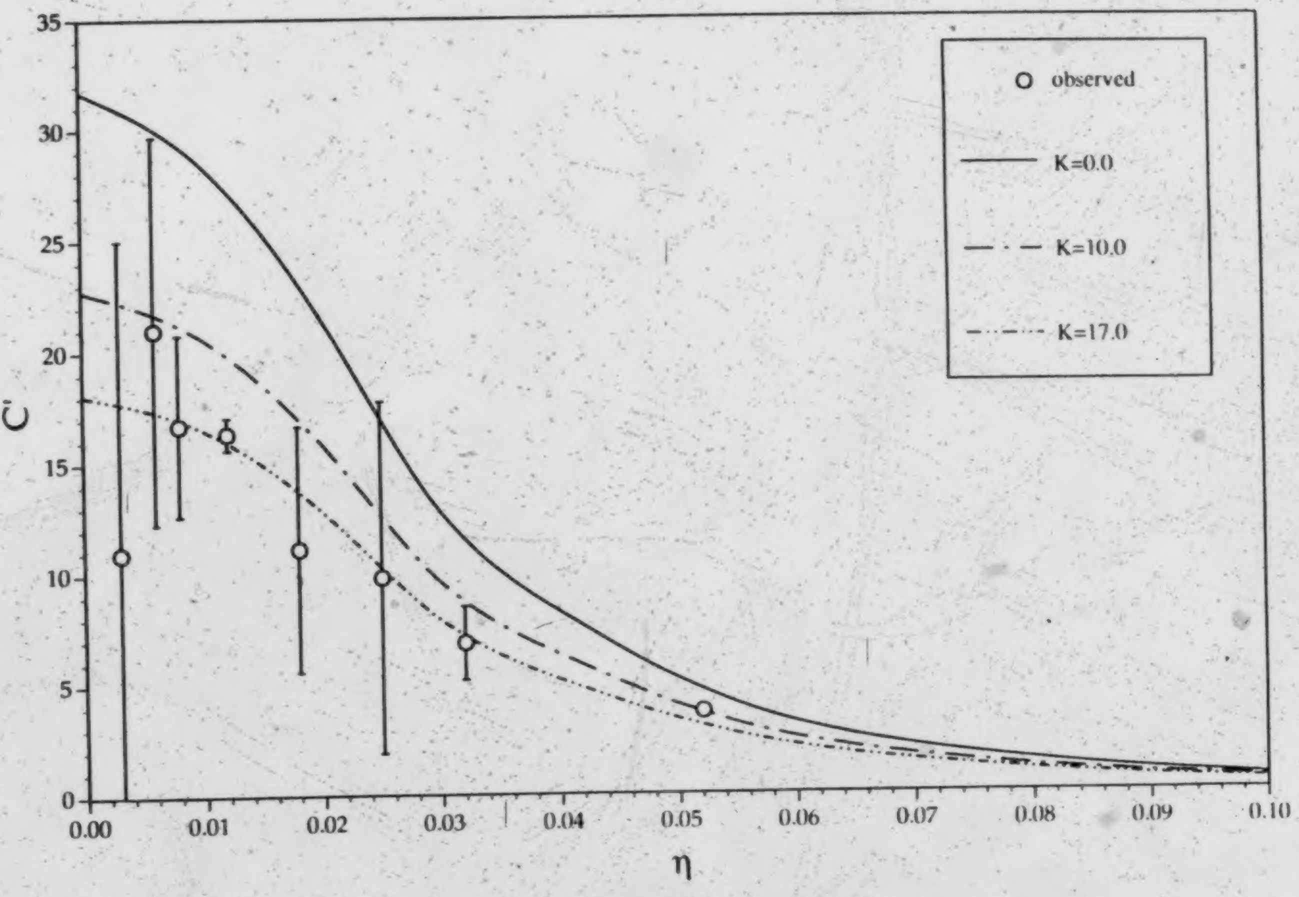


Figure 6.15 Model predictions of TRC distribution at E.L. Smith cross section 3 for various decay coefficients.

statistical theory, it is commonly used to allow for interpretation of censored data (Helsel, 1990) and the use of a more sophisticated distributional or robust method was precluded by the lack of additional data. The resulting estimate is conservative as it is biased towards a value higher than the true concentration.

Data collected in field investigations is often less precise than that which could be expected from a laboratory study. Uncertainties in many parameter estimates, and the inability to predict or control natural events usually results in considerable scatter in field data. However, this lack of precision does not necessarily imply a reduction in accuracy. Conversely, field studies are much better able to simulate the complex processes occurring within the environment. A first-order decay coefficient for TRC of 17.0 d^{-1} provides a very good overall fit to the observed data, passing through the 95% confidence intervals of all samples (Figure 6.15). Figure 6.15 suggests that a reasonable lower bound on the first-order TRC decay coefficient during this study period is provided by selection of $k = 11.0$ d^{-1}. All observed data points fall below the predicted concentration profile, providing a conservative estimate of k.

Data from the night sampling of the chlorine plume provided similar results to that seen in the day-time samples. Presentation and analysis of this data will be reserved for Section 7.2.2.2 in the Discussion.

6.2.3 Microbiological Tests

Similarly to the Rossdale field study, microbial samples were also collected within the E.L. Smith chlorine plume. The resulting data are summarized in Figures 6.16a to 6.16c for total heterotrophs, total coliforms and fecal coliforms respectively. Collected data is also provided in Appendix F. It should be noted that fecal coliform counts exceeded total coliform counts in the 6 and 9 m samples at cross section 4. This would not normally be expected, and suggests that these samples may have been contaminated.

A more striking contrast was observed between near-bank and main-flow microbial samples collected in the E.L. Smith study than was observed downstream of Rossdale. Fewer sewer outfalls were located along this length of the river, reducing unquantified inputs somewhat. However, several small streams and surface runoff was observed along the riverbank, which may have provided considerable non-point source input. Again, the data is intended for qualitative inspection only.

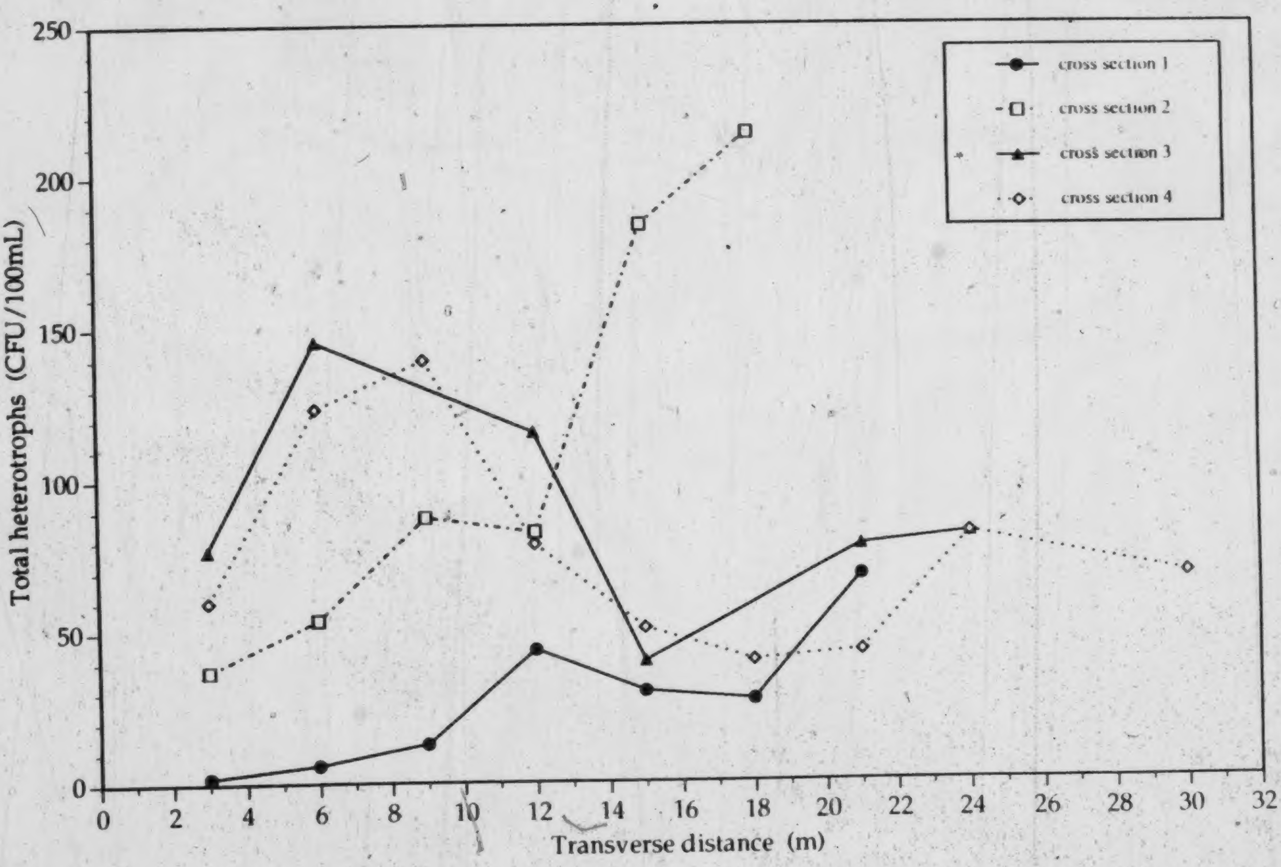


Figure 6.16a Total heterotroph distribution in the E.L. Smith chlorine plume.

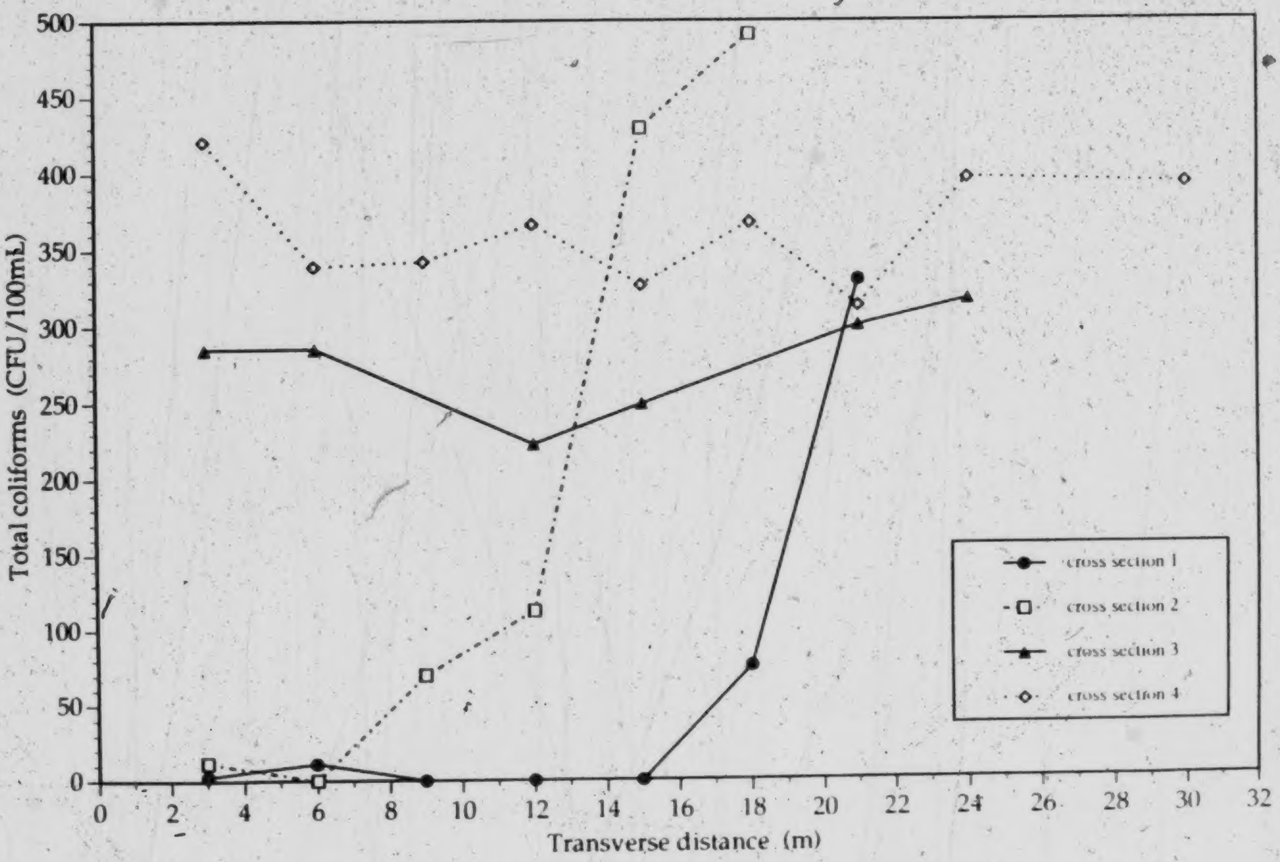


Figure 6.16b Total coliform distribution in the E.L. Smith chlorine plume.

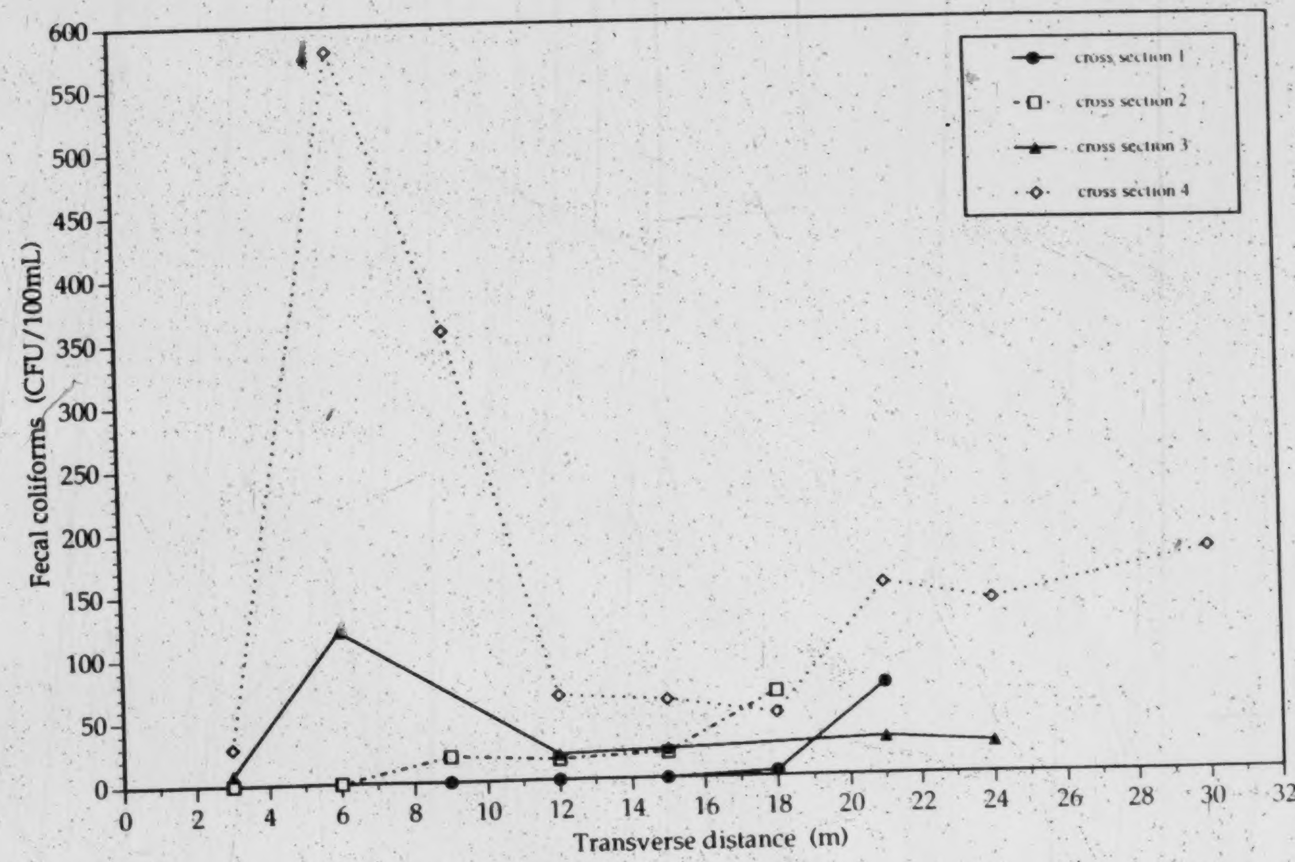


Figure 6.16c Fecal coliform distribution in the E.L. Smith chlorine plume.

6.2.4 Benthic Chlorine Demand Study

A series of batch benthic chlorine-demand tests were conducted at the E.L. Smith outfall on October 11 1990, and an additional series was performed on July 10, 1991. The intent of these studies was to obtain a preliminary estimate of the contribution of the benthic demand to the overall rate of chlorine decay. Past research has indicated that a considerable demand for in-stream pollutants may be exerted from the benthos, and consideration of the uptake rate for chlorine may be important in determining the overall fate of discharged chlorine.

The experimental procedure and sample analysis method for his test was discussed in Section 4. To avoid contamination of the experimental set-up by plant discharge waters, the October tests were conducted immediately upstream of the plant outfall. The bed composition in this area was representative of downstream conditions, except that it had not received any prior exposure to residual chlorine. The general flow and water quality conditions were similar to those found during the chlorine plume test. Table 6.7 summarizes water qualities within the North Saskatchewan River for the chlorine plume study date of September 26, 1990, and at the time of the benthic studies on October 11, 1990 and July 10, 1991.

Three separate experiments were conducted, two using the same initial chlorine dose, and the third using a dose approximately 2.5 times higher. Results from the three independent tests are summarized in Figure 6.17. The data plot as a linear relationship using a semi-logarithmic scale, indicating that the reaction kinetics are first-order. A second-order fit was also attempted, but the data did not follow this relationship. First-order decay rate coefficients of 591, 584, and 448 d^{-1} were observed. These represent the rates of decay of a total chlorine residual. As chlorine was added as NaOCl, some free chlorine may have been present within the residual.

Comparison of the above k values with the overall decay rate determined through the mixing analysis indicates that the benthic demand was an order of magnitude higher than the overall decay rate. However, no apparent error source was available to explain the high decay rates seen in these studies. Inspection of Figure 6.17 indicates that the results were reproducible over the range of initial concentrations tested. This suggests that the mixing, sampling, and analysis procedures were adequate. No air was permitted inside the sealed reaction chamber, eliminating the possibility of TRC loss through volatilization. The

Table 6.7. Water quality parameters in the North Saskatchewan River during benthic demand studies.

Parameter	September 26, 1990	October 11, 1990	July 10, 1991
pH	8.3	8.2	8.3
Temperature (°C)	14.2	6.0	18.0
Turbidity (NTU)	5.0	4.0	135
U.V. absorbance (@ 200 nm)	4.4	4.2	13
volatile organic carbon (mg/L)	< 0.001	0.001	< 0.001
colour (TCU)	4.0	3.0	30
Total hardness (mg/L as $CaCO_3$)	155	161	144
Total alkalinity (mg/L as $CaCO_3$)	126	124	128

Source: City of Edmonton (1990)

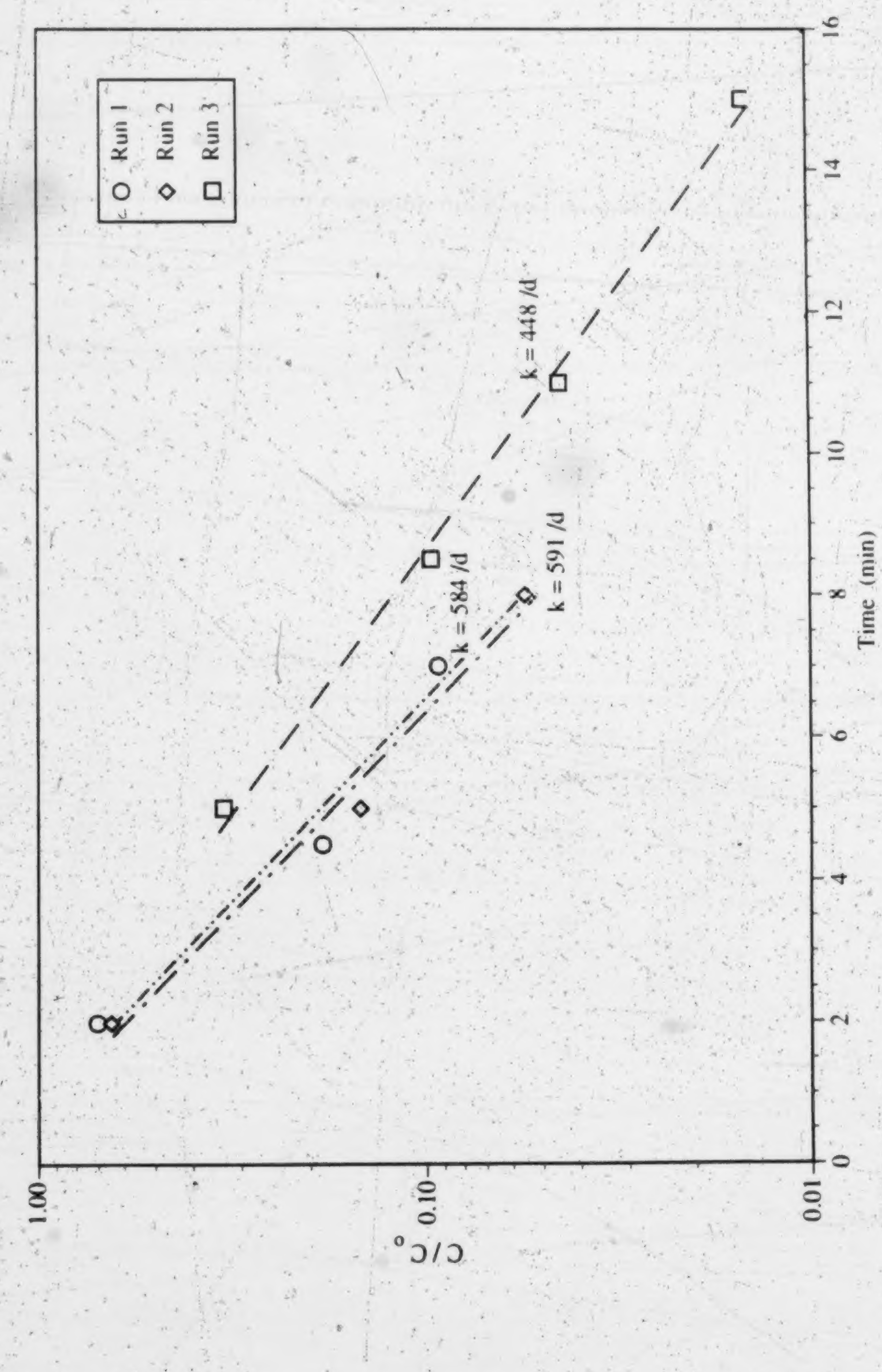


Figure 6.17 TRC consumption by benthic chlorine demand: October, 1990.

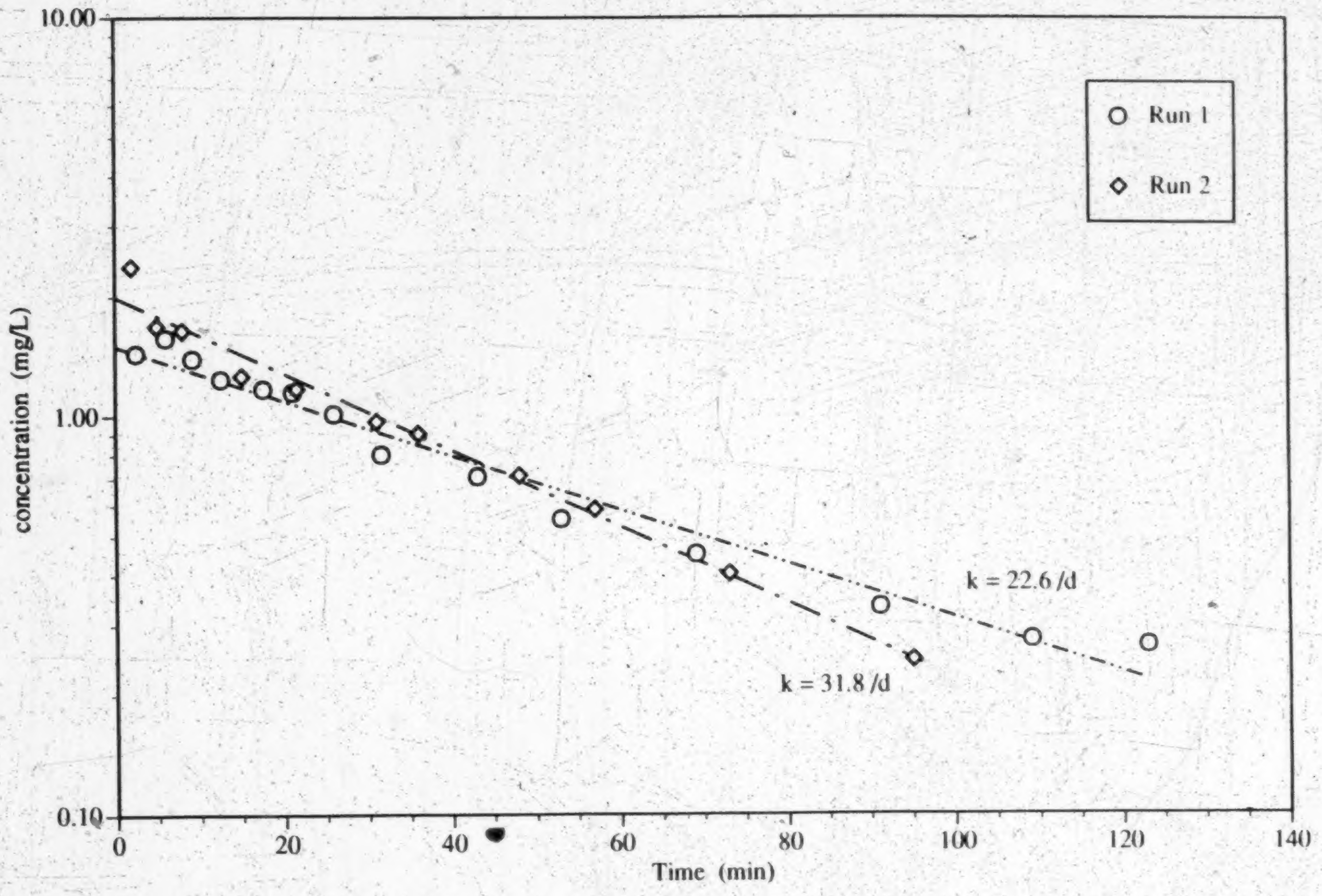


Figure 6.18 TRC consumption by benthic chlorine demand: July, 1991.

sediment-side of the the chamber was buried at least 10 mm into the bed, eliminating any water exchange or flushing of the chamber.

To confirm the results obtained from the October 1990 tests, two additional experiments were conducted at the E.L. Smith plant on July 10, 1991. Two objectives were identified for these tests: the first objective was to obtain a comparison of the benthic uptake rates for TRC between different water qualities by comparison with the October results, and the second objective was to determine whether the rate of TRC uptake by the benthos was affected by previous exposure to chlorine. The first experiment was performed at the outfall, where the sediments had received prior intermittent exposure to chlorine residuals. The second experiment was performed approximately 200 m upstream from the outfall, over sediments which had received no previous chlorine exposure.

The experimental procedure used during the July 1991 tests was the same as that used in the October 1990 experiments. Results from the July experiments are presented in Figure 6.18. First-order decay of TRC was observed, and a decay rate coefficient of 22.6 d^{-1} for the test location with previous chlorine exposure was observed. The second experiment, where the sediments had not been exposed to any chlorine residual yielded a slightly faster decay coefficient of 31.8 d^{-1}.

6.3 Laboratory Investigations of Water Column Chlorine Demand

Estimates of the water column chlorine demand were obtained from three experiments conducted using North Saskatchewan River water. A sample of raw water from the Rossdale Water Treatment Plant was obtained on September 15, 1990, and two samples from E.L. Smith were collected on September 23 and October 4. The water was spiked with a concentrated solution of NaOCl, to provided initial TRC concentrations ranging from 2 to 4 mg/L, and chlorine decay was monitored with time. The results from these experiments are plotted in Figure 6.19. First-order decay of TRC was observed in all of the water samples, with decay-rate coefficients ranging from 2.5 to 3.7 d^{-1}.

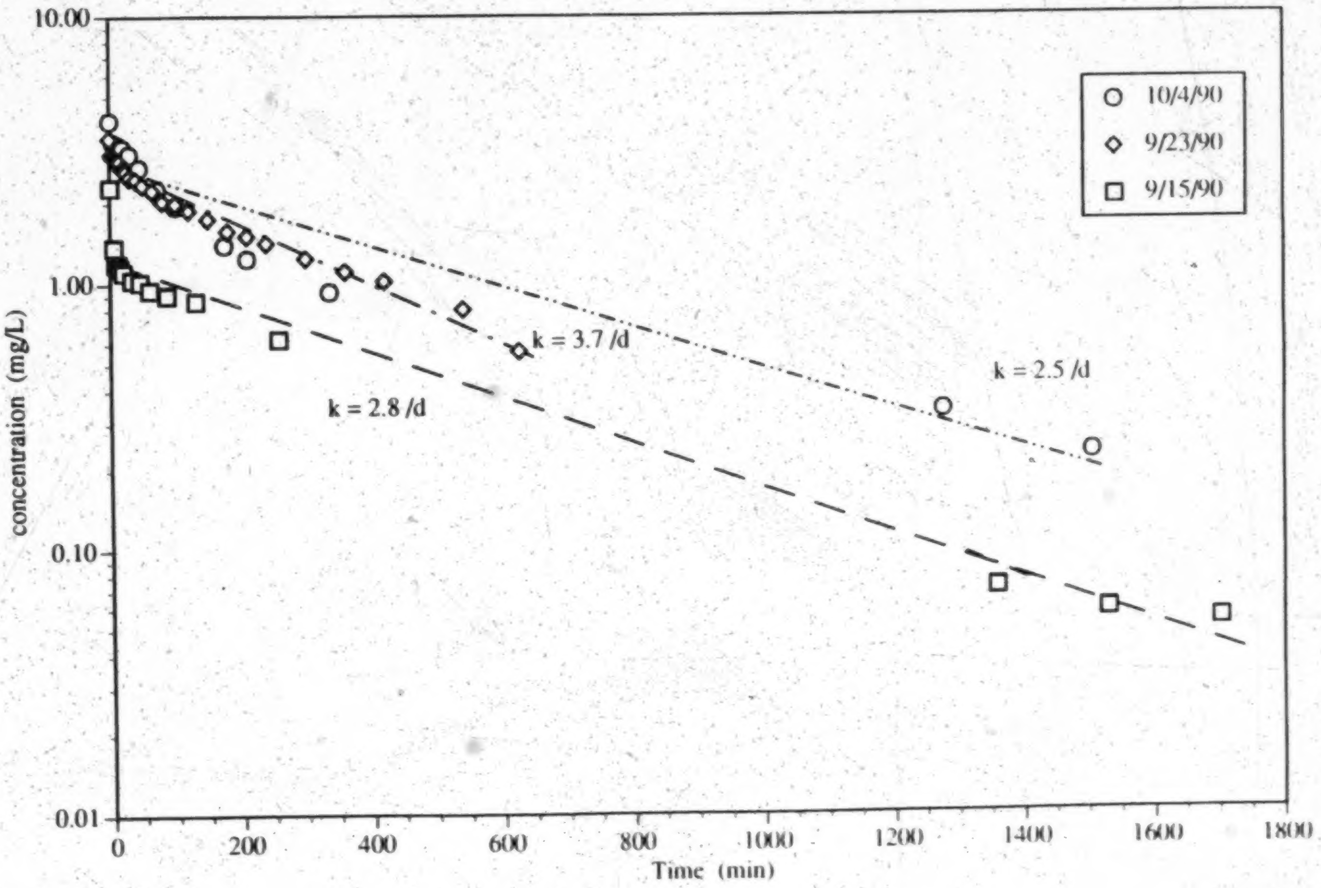


Figure 6.19 Water column chlorine demand in North Saskatchewan River water.

7.0 Discussion

7.1 Transverse Mixing

Results from the Rhodamine WT tracer studies have shown that significant transverse concentration profiles exist over the extent of the chlorine plumes downstream from bank discharges at the Rossdale and E.L. Smith Water Treatment Plants. Within this region, the two-dimensional mixing behaviour of the effluent plume must be considered to obtain an accurate assessment of pollutant decay rates. The dye tracer studies provided information on the mixing properties of the North Saskatchewan downstream from the water treatment plants. The tracer studies were conducted over a length of river 1 to 2 km beyond the point where residual chlorine was detected . Although this information was not required for assessment of the chlorine decay rates, it would be useful for purposes of subsequent modelling, and was therefore included in this discussion.

Analysis of the field data downstream from the Rossdale Water Treatment Plant indicated a large variability in the magnitude of the transverse mixing coefficient. Values of E_z obtained downstream of each cross section ranged from 0.0156 m^2/s at the upstream end to 0.893 m^2/s at the end of the study reach. Variations in the transverse mixing coefficient of the magnitude observed in the Rossdale tests have been seen in other field studies involving bank discharges into large rivers (Putz, 1983), and are indicative of the variable flow conditions in the North Saskatchewan over the study reach, especially along the near-bank area. Values of E_z observed during the E.L. Smith study show much less variation, and ranging from 0.0173 to 0.0800 m^2/s, are generally smaller than those obtained downstream of Rossdale.

The high degree of variability seen in the transverse mixing coefficients downstream of Rossdale may be explained by consideration of the flow properties of the North Saskatchewan through this section, and by understanding the physical significance of the transverse mixing coefficient. The transverse mixing coefficient as defined in Equation 2.18, and as used throughout this analysis, incorporates the combined effects of turbulent transverse diffusion and transverse dispersion due to the presence of any mean transverse velocities. As E_z implicitly accounts for transverse dispersion due to secondary currents, it would be expected that it would increase in highly sinuous, curved channels where substantial secondary currents would be expected to develop (Beltaos, 1978). Downstream from the Rossdale discharge, as can be seen from Figure 5.3, several severe bends occur over a short distance. Inspection of the cross section profiles provided in Appendix A also show migration of the thalweg across the channel. These observations suggest that substantial transverse velocities may be present within this area. These secondary flows would have the effect of increasing the value of the transverse mixing coefficient as transverse dispersion would be increased. As the additional mixing resulting from these secondary currents is implicitly accounted for in the transverse mixing coefficient, the model was able to successfully predict the tracer distribution over this region.

At E.L. Smith, the reach over which the tracer study was conducted is characterized by a single, large bend, which changes the major direction of flow by more than 205° in less than 3 km. TRSMIX was able to accurately predict the tracer concentration to cross section 3, at 1270 m. Downstream of this cross section, the predicted concentrations were lower than the observed concentrations along the near-bank zone by approximately 20%. Agreement between the model and observed concentrations improved at greater distances off of the bank. Although the model was unable to accurately predict the magnitude of the tracer concentrations at cross sections 4 and 5, the most important factor, the slope of the concentration - cumulative discharge curve was maintained. The mixing coefficient is a function of the variance of this curve, which is dependent on the slope. As the slope of the curve was adequately maintained, the resulting mixing coefficients should be accurate.

The slight variation between the predictions of the numerical solution and the observed dye profile at E.L. Smith did not become significant until cross section 4. The primary purpose of the tracer studies was to provide a conservative datum which could be used to determine the extent of chlorine decay. For both tests, residual chlorine was detected no further downstream than cross section 4; a length over which the mixing behaviour was accurately modelled. Therefore, although some problems in predicting the stream mixing behaviour did exist at E.L. Smith, this would not be expected to impact on the assessment of chlorine decay rates as these problems occurred at points downstream from the chlorine plume.

Previous mixing investigations in the North Saskatchewan River near Edmonton have reported transverse mixing coefficients similar to those found in the E.L. Smith study. Beltaos and Anderson (1979) reported a reach-averaged value for E_z of 0.0216 m^2/s for the North Saskatchewan River from Clover Bar to Wasketenau (immediately downstream from Edmonton). However, they also noted that significant deviations from the reach-averaged value occurred over relatively short distances. The value reported by Beltaos and Anderson is lower than most reported in natural streams (Fisher et al., 1979). Beltaos and Anderson (1979) noted that where large bends in the river occurred, the apparent mixing coefficient increased significantly and suggested that the reason for the low value of 0.0216 m^2/s may have been a result of the relatively straight and uniform geometry of the river below Clover Bar. The site of the Rossdale test was characterized by a highly sinuous channel, which would have the effect of increasing the apparent transverse mixing coefficient.

Comparison of the mixing ability of the North Saskatchewan River with other streams is best facilitated by consideration of the mixing coefficients in a dimensionless form. As discussed, no universally accepted method has yet been found for presentation of dimensionless mixing coefficients. The size of the turbulent eddies which best characterize the mixing processes within the stream have previously been scaled using properties of the stream such as the width, depth, or hydraulic radius, or properties of the plume such as the half-plume width. The observed mixing coefficients from the field tests performed in this study, non-dimensionalized using each of the above length scales, are presented in Tables 7.1 and 7.2. As the tests were conducted under open-water conditions, the hydraulic radius and the mean stream depth are equivalent, and only dimensionless mixing coefficients based on the channel depth are presented.

Beltaos and Anderson (1979) reported a value of $\frac{E_z}{hu_*}$ under similar flow conditions of 0.17 on the North Saskatchewan River below Clover Bar. This study found the values to be somewhat higher downstream of E.L. Smith. The same parameter downstream of Rossdale showed considerable variation, with much larger values being observed.

Presentation of the transverse mixing coefficient in a non-dimensional form should yield a relatively constant mixing coefficient along the length of the plume. Tables 7.1 and 7.2 indicate that none of the length scales selected adequately transform the data to achieve this goal. Considerable scatter is evident in all of the coefficients, with $\frac{E_z}{hu_*}$ varying over the widest range. Use of either the half-plume width or the mean channel width reduces the scatter somewhat, but the data still spans two orders of magnitude.

The difficulty in finding a length scale suitable over the length of the entire plume may imply that the appropriate length scale varies with longitudinal position in the plume. For the specific case of a bank discharge into a wide river, Putz (1983) found in a mixing study in the ice-covered Slave River that $\bar{b}$ was the best length scale at $\bar{b}/W < 0.35$. At ratios of $\bar{b}/W > 0.35$, W proved to be the most appropriate length scale. A similar relationship was not observed under open water conditions, perhaps due to

Table 7.1 Tracer plume and river characteristics downstream of Rossdale Water Treatment Plant (September 5, 1990).

cross section	distance (m)	u_* (m/s)	B (m)	H (m)	$\bar{b}$ (m)	E_z (m^2/s)	$\frac{E_z}{wu_*}$	$\frac{E_z}{hu_*}$	$\frac{E_z}{\bar{b}u_*}$
1	110	0.096	130	2.31	2.8	0.0156	0.001	0.070	0.058
2	640	0.056	167	1.19	12.0	0.0403	0.004	0.605	0.060
3	1400	0.062	140	1.68	7.5	0.2840	0.033	2.727	0.611
4	2370	0.028	180	1.48	37.5	0.4620	0.092	11.15	0.440
5	3420	0.077	168	1.69	72.5	0.8930	0.071	6.862	0.160

Table 7.2 Tracer plume and river characteristics downstream of E.L. Smith Water Treatment Plant (September 25, 1990).

cross section	distance (m)	u_* (m/s)	B (m)	H (m)	$\bar{b}$ (m)	E_z (m^2/s)	$\frac{E_z}{wu_*}$	$\frac{E_z}{hu_*}$	$\frac{E_z}{\bar{b}u_*}$
1	125	0.082	137	0.98	1.0	0.0173	0.002	0.214	0.210
2	465	0.034	143	1.66	4.5	0.0328	0.007	0.569	0.210
3	1270	0.076	132	2.42	14.0	0.0847	0.008	0.463	0.080
4	1750	0.085	162	1.28	12.0	0.0507	0.004	0.469	0.050
5	2445	0.156	160	2.67	20.0	0.0800	0.003	0.192	0.026

insufficient data beyond 0.35W. Based upon the available data, no 'best' length scale or relationship for non-dimensionalizing the transverse mixing coefficient is apparent from this study.

7.2 Chlorine Decay

7.2.1 Gross Rate of Chlorine Decay

Following the mixing analysis, the effects of dilution on the in-stream concentration of residual chlorine within the discharges was accounted for. The mixing data was then used as a conservative datum, and any difference between the observed chlorine concentrations and the concentration profiles predicted by the numerical model were attributed to a decay of chlorine within the receiving stream. In this manner, the overall in-stream rate of chlorine decay was determined. The decay rate coefficients obtained from this analysis represented the gross rate of reduction of total residual chlorine within the receiving stream attributed to all mechanisms but dilution. These rate coefficients indicated the rate at which TRC was being removed from the stream, but they provided no indication of the ultimate fate of the chlorine residuals, nor of the processes governing the decay. By supplementing the plume tests with additional field and laboratory investigations, an improved understanding of the processes affecting chlorine decay within receiving streams was obtained.

Over the reach in which detectable levels of residual chlorine were observed, the mixing behaviour was quite well defined, and as was seen in Figures 6.4 and 6.12, TRSMIX was able to successfully predict the tracer profiles. The in-stream rates of chlorine decay were then determined by numerically predicting the chlorine profiles and selecting the first-order decay rate coefficient which provided the best visual approximation to the observed data.

Determination of the chlorine decay rate coefficients by numerical methods necessitated that several simplifying assumptions be made. First, the in-stream rate of chlorine decay was assumed to follow a first-order relationship. This would require that the dominant processes influencing the decay rate were first-order. Previous investigations of chlorine decay in wastewater treatment plant effluent plumes have found that chlorine concentrations can generally be described as a first-order process (Heinemann et al., 1981; Lee et al., 1982; Gowda, 1981). This assumption was further confirmed by the mass balance on chlorine flux downstream of Rossdale, where the data did follow a first-order relationship (Figure 6.7). The decay coefficient was also assumed to be constant throughout the plume. Although no previous data is available to validate this assumption, it tends to be supported by consideration of the physical and chemical factors which govern the rate of chlorine decay. Such factors as water column demand, rate of volatilization, and benthic uptake rates are predominantly a function of the river environment. Considering the relatively short length of the chlorine plume, a significant variation in these parameters would not be expected to occur.

As decay within the plume follows a first-order relationship, the greatest change in concentration occurs at the points of highest concentration, and for the case of a bank discharge, the near-bank points should therefore receive the greatest weighting in selection of the optimum k value. This generalization is complicated somewhat by the presence of stagnant pools along the bank, which may retard the downstream flow of water immediately adjacent to the bank, and residual chlorine at these points may have actually been in the system for a longer duration than would be calculated based on consideration of the near-bank velocity field. In both the Rossdale and E.L. Smith studies, the point adjacent to the bank was seen to yield a lower chlorine residual than the next sample point off of the bank. These samples therefore may not represent the bulk system, and their validity should be carefully considered in interpretation of the data.

The 90% and 95% confidence intervals were plotted for the Rossdale and E.L. Smith chlorine plume data respectively. Due to the limited number of samples collected, and the scatter seen in the data, the confidence intervals on the Rossdale data bracket a wide range of chlorine concentrations. A 90% level of significance was selected for these data, as only 2 degrees of freedom were available for most points, and the use of a more restrictive level of significance would result in such wide confidence intervals that the physical meaning of the data would be lost. The wide standard deviations observed on some of the data points does not imply problems with the analytical techniques, but instead indicates the natural variability to be expected in sampling of this type. Especially along the bank, considerable variation in the chlorine concentrations would be expected. The variable hydrography along the bank gives rise to visible swirling eddies, which can result in wide fluctuations in individual sample concentrations. While it may be possible to attain a relatively good estimate of the mean concentration with only a few samples, the physical behaviour of the system often precludes the possibility of attaining a standard deviation that would be considered acceptable in a laboratory investigation.

Downstream from the Rossdale Water Treatment Plant, a decay coefficient of 26.0 d^{-1} provided the best overall fit to the data (Figure 6.8) and passed through the error bars for every sample. However, this under-estimated the observed concentration at $\eta=0.02$, and a k of 10.0 d^{-1} provided a much improved fit to this data point. Use of $k = 10.0\ d^{-1}$ does not provide a good overall fit to the data, and does not provide a close estimation of the concentrations at the near-bank points; however, it does represent a reasonable lower-bound on the decay rate. Correcting these decay rates to a standard temperature of 20 °C, and using Equation 2.12 with a value for θ of 1.03 (Gowda, 1978), the best-fit and lower-bound decay rates are 28 d^{-1} and 11 d^{-1} respectively.

Data on the E.L. Smith chlorine plume collected at cross section 3 did not exhibit as high of a variation as was seen with the Rossdale plume. This allowed the use of confidence intervals at a 95% level of significance for all points where sufficient replicate samples were available. A best fit to the data was obtained with $k = 17.0\ d^{-1}$ (Figure 6.15). The predicted concentration distribution was very close to the observed distribution, and passed within the 95% confidence limits of every sample. One data point, at $\eta = 0.06$, fell above the profile predicted with $k = 17.0\ d^{-1}$. The use of $k = 11.0\ d^{-1}$ bracketed this point, but over-estimated the concentrations at all other sample points. For the E.L. Smith plume study, $k = 11.0\ d^{-1}$ could therefore be accepted as a lower-bound on the chlorine decay rate. Corrected to standard temperature, these represent decay rates of 20 and 13 d^{-1} respectively.

Values of the first-order total chlorine decay coefficient observed in the two field studies fall within the broad range previously reported (Table 4.3). Direct comparison of the results obtained in this study with those of previous researchers is difficult due to the lack of available field data on water treatment plant discharges. Effluent plumes downstream from chlorinated wastewater treatment plants have received slightly more attention, and some data from field investigations does exist. The relatively large amounts of organic material present in these discharges suggests that a greater proportion of the TRC in these discharges will be composed of chlorinated organics, which may be more persistent within the environment. However, the greatest proportion of these residuals is probably still comprised of chloramines, and the difference in the in-stream decay rate between wastewater treatment and drinking water treatment plant discharges would not be expected to be great. The water quality and morphological characteristics of the receiving stream would have a greater impact on the decay rates than a small change in the speciation of residual chlorine.

In summer field investigations conducted in Aurora Creek, Ontario, Gowda (1978) reported first-order TRC decay rates of 17.2 to 39.8 d^{-1}. The two rates reported represented subsequent reach sections, and a value of 17.2 d^{-1} was selected to be representative of the reach as a whole. The discharge in Aurora Creek during these tests was 0.22 m^3/s. This analysis was based upon an assumption that the effluent was completely mixed across the 3.5 m wide, 0.26 m deep stream. This assumption may not be completely valid, but the plume was observed to spread completely across the channel in approximately 90 m, and transverse concentration differences of less than 10% were observed within 500 m downstream of the outfall. Gowda (1978) therefore represented the chlorine distribution at each transect as a mean value. Although the results of Gowda (1978) may not be directly comparable to the conditions of this study, they do provide a useful grounds for comparison. Chlorine decay rates observed in this study agree closely with those observed in Aurora Creek, and the differences observed may result from differing water qualities, effluent compositions, and stream conditions.

Gowda (1978) also conducted field studies into chlorine decay on the Boyne River, Ontario. In this larger river ($Q = 0.78$ m^3/s), complete-mixing of the effluent across the river could not be assumed. The mixing behaviour of the plume was modelled using analytical techniques, and the decay rate was obtained by subtracting the concentration decrease predicted by consideration of the dilution ability of the stream from the overall observed chlorine decay. Results from this study suggested that the first-order decay coefficient ranged from 36.9 to 125 d^{-1}. Gowda selected a reach averaged value of 36.9 d^{-1}. The accuracy of these estimates may not be as great as the study in Aurora Creek due to the non-site specific mixing analysis. However, the data is still valid, and provides a good estimate of the rate at which TRC was decaying in the Boyne River at the time of the test.

A more recent study of TRC decay downstream from a municipal wastewater treatment plant in Lampson Brook Massachusetts was reported by Reckhow et al. (1990). They measured concentration profiles over a distance of 120 m below the outfall, and found a gross first-order TRC decay coefficient of 144 d^{-1}.

Direct comparison of the rate of decay of residual chlorine obtained in this study with values reported in other water bodies would indicate that TRC decay rates are generally not as rapid in the North Saskatchewan River. Variations in the water qualities of the individual streams may have contributed somewhat to the differences, but the greatest difference may be due to the much larger size of the North Saskatchewan River. Rates of volatilization and benthic uptake scale inversely on channel depth, and as these represent important removal mechanisms, the rate of chlorine depletion would be expected to decrease in a larger, deeper river. The differences observed between Gowda's (1978) results in Aurora Creek and the Boyne River, those of Reckhow et al. (1990) and the results of this study indicate the site-specific variations to be expected in the rates of decay of residual chlorine within the receiving environment.

7.2.2 Chlorine Decay Pathways

Field studies of the in-stream decay of residual chlorine, as reported above, are the most accurate method to determine the actual decay rates of residual chlorine within the receiving environment. The results obtained from these studies are superior to laboratory based analyses, as they provide exact simulation of the receiving water body, and no modelling errors are introduced. One limitation of this method of analysis is that it provides no indication of the relative degree to which the many possible decay mechanisms contribute to the overall rate of chlorine decay. For a simple investigation, where the primary objective is only to determine approximate decay rates, one plume study may provide sufficient information. However, it is often desirable to predict the effect that changing environmental conditions may have on the in-stream rate of decay. This can only be achieved by supplementing the information obtained in the field with observations made from laboratory studies, where individual decay mechanisms can be isolated, and the rates and sensitivity of these individual processes can be studied under controlled conditions.

7.2.2.1 Water Column Chlorine Decay

Results from the study of water column chlorine decay in three samples collected from the North Saskatchewan in late September to mid-October, 1990 showed first-order TRC decay coefficients of 2.5 to 3.7 d^{-1} (at 20 °C). These values indicate only the rates of chlorine decay due to decomposition and chemical reaction, as decay mechanisms such as UV decomposition, benthic uptake, and volatilization were eliminated. Water quality at this time was relatively good, with the total organic carbon content of the river water ranging from approximately 1.7 to 3.0 mg/L. The decay rates observed in these samples compare well with water column decay rates reported with surface waters of similar quality (Reckhow et al., 1990; Lee et al., 1982; Heinemann et al., 1981).

The rate of decay of TRC attributable to chemical reactions within the receiving water matrix represent approximately 9 to 22% of the overall rate of chlorine decay observed in this study. Relative contributions of this magnitude were also observed by Heinemann et al. (1981). Water column chlorine demand values are relatively easily to quantify in the laboratory, and are therefore often used to estimate the rate of chlorine decay within the receiving waters. Based on the results of this study, it appears that such an approach may neglect several important chlorine removal mechanisms, and result in an overly conservative estimate of chlorine decay within the environment. Although chlorine decay through water column reactions is an important decay mechanism, it does not appear to be the dominant one.

7.2.2.2 Photolytic Chlorine Decay

Night-time chlorine residual measurements in the E.L. Smith plume enabled collection of chlorine residual data within the North Saskatchewan River under conditions in which the effects of UV photolysis on TRC decomposition would be minimized. The results of this study are shown in Figure 7.1 and 7.2, where the concentration profiles at cross sections 3 and 4 are plotted for both the day-time and night sampling. Limited manpower and equipment precluded complete repetition of the day-time sampling routine. Selected points at the furthest downstream locations were sampled, as the greatest difference should be observed at sites representing the largest exposure times. To determine whether a statistically significant difference between the two sample sets existed, a paired t-test was performed on the data, and the results presented in Table 7.3. At a 95% level of significance, no statistical difference existed between the two sample sets. Visual inspection of Figures 7.1 and 7.2 confirm this conclusion, as very small differences between the two sample sets are generally observed. This suggests that photosynthetic decay does not contribute significantly to the decay of chlorine within the North Saskatchewan River.

An understanding of the role of photosynthesis in the decay of residual chlorine within the receiving stream is important not only for night discharges, but is also required so that the effects of an ice-cover, which will greatly retard UV radiation, may be understood. Several authors have cited photolytic demand as a significant contributor to the overall rate of chlorine decay (Dotson and Helz, 1984; Lin et al., 1983; Jolley and Carpenter, 1983; White, 1986). However, most of these researchers conducted laboratory studies, where the effects of other decay processes may have been reduced or eliminated. Recently, several investigations of chlorine decay, using light-bottle dark-bottle or similar tests, have found that photosynthetic decomposition has little effect on the overall rate of chlorine decay (Lee et al., 1980; Heinemann et al., 1981; Abdel-Gawad and Bewtra, 1988; Reckhow et al, 1990). These authors found that processes such as volatilization had a much greater impact on the overall rates of chlorine depletion. The results of this study agree with the later group of researchers, and suggest that photo-decomposition contributes insignificantly to the gross rate of chlorine decay in natural streams.

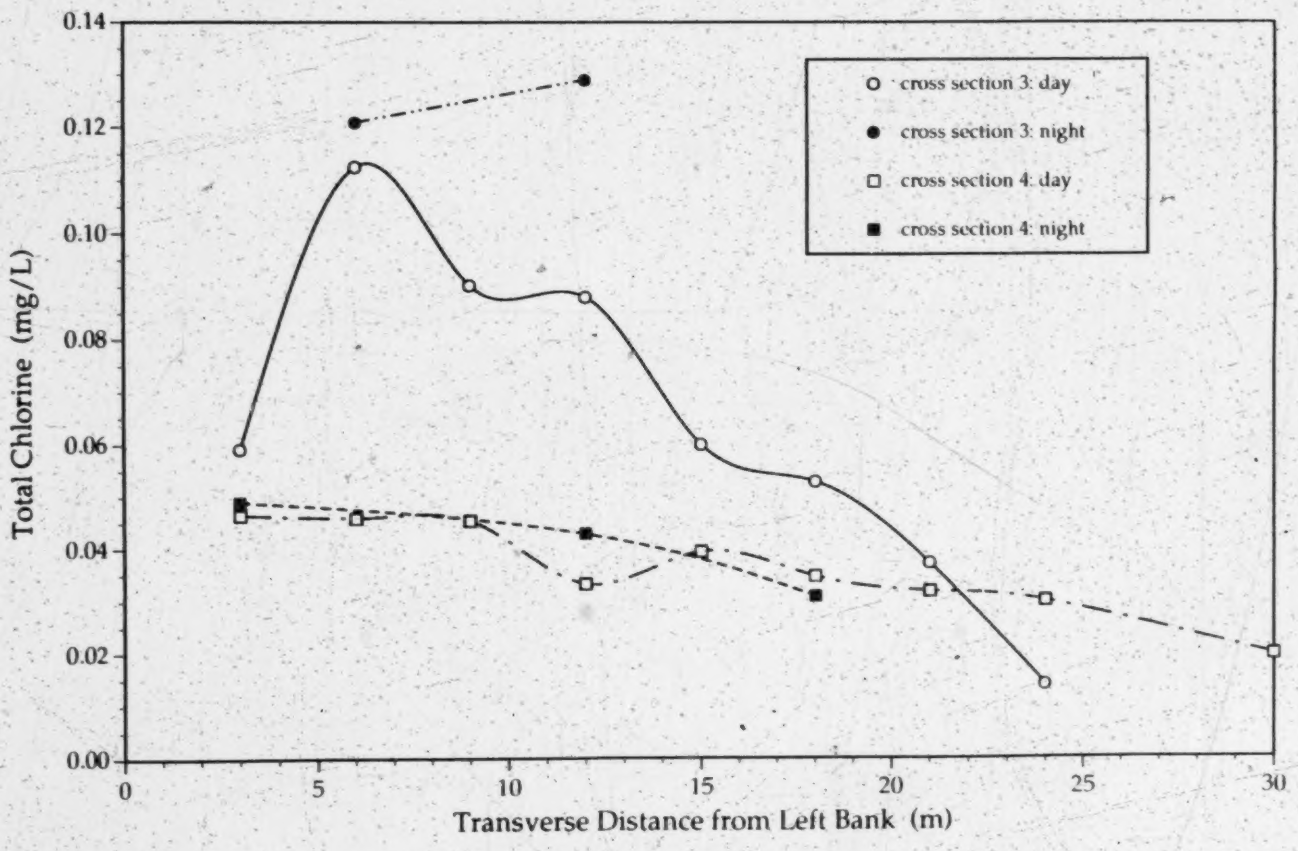


Figure 7.1 Comparison of day-time and night-time residual chlorine concentrations in E.L. Smith plume.

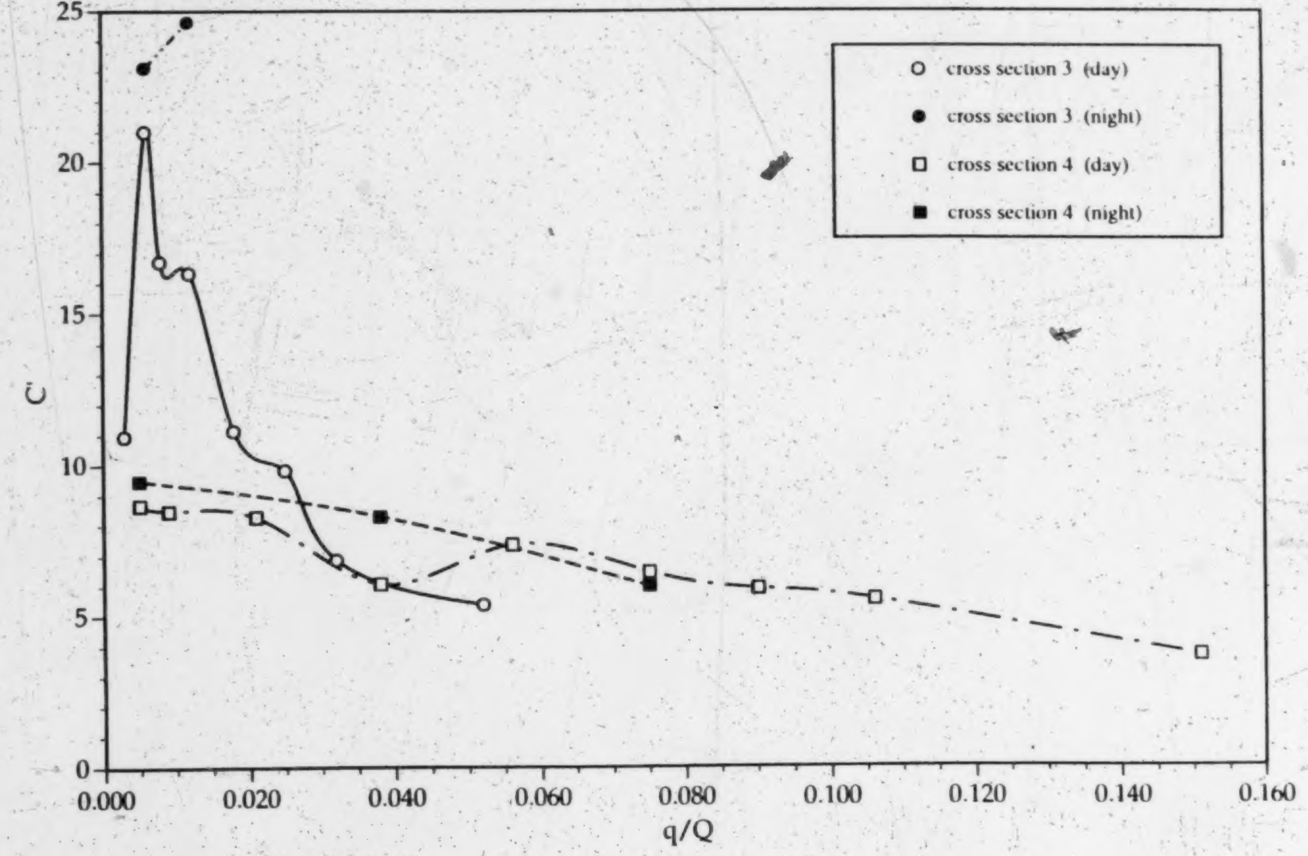


Figure 7.2 Dimensionless comparison of day and night-time residual chlorine profiles in E.L. Smith plume.

Table 7.3 Paired t-test examining effects of photosynthesis on chlorine decay in E.L. Smith plume.

Cross section	$\bar{x}$	$s_{\bar{y}}$	v	t	$t_{0.95,v}$	significant difference
3	0.025	0.017	1	1.47	12.706	no
4	0.008	0.004	2	0.750	4.303	no

7.2.2.3 Benthic Chlorine Demand

Attempts to quantify the benthic uptake rate for TRC provided some interesting, yet inconclusive data. Two series of experiments were conducted at the E.L. Smith Plant, one on October 10, 1990 and one on July 11, 1991. These tests, as discussed in Section 6.2.4, followed first-order decay kinetics, but yielded widely varying values for the benthic uptake rate. The benthic uptake experiments conducted in this study were designed to provide an order-of-magnitude estimate of the chlorine uptake rate, and were not intended to provide definitive rate constants. The use of batch experimental apparatus for the determination of the kinetics of benthic pollutant uptake may not completely simulate the physical behaviour of the system. Limitations similar to those cited by Belanger (1981) for the study of benthic oxygen uptake could be expected with chlorine uptake: the batch system does not simulate the natural conditions as no flow exists; the sediments are not given sufficient time to acclimate to the concentration of chlorine present; prior chlorine exposure is difficult to quantify; and the extremely heterogenous nature of the sediments is not easily modelled.

Experiments conducted in October 1991, soon after the chlorine plume study resulted in apparent chlorine decay / uptake rates which, after correction for water column decay and corrected to standard temperature, ranged from 691 to 888 d^{-1}; an order of magnitude greater than the overall rate of chlorine decay observed in the plume study. To reduce the possibility of contamination from plant discharge waters, the apparatus was located immediately upstream of the plant in sediments which were visually similar to those observed downstream of the outfall. A series of three replicate experiments were performed, with the chamber being emptied and moved slightly following each test. Similar trends in the data were observed in all tests, suggesting that test-to-test reproducibility was good, and eliminating leaks or other obvious experimental errors as a source of the high decay rates.

Two further benthic uptake tests were conducted on July 10, 1991 to obtain additional data on benthic chlorine demand kinetics. One run was conducted in an area which had received prior chlorine exposure, and one run was conducted in sediment which had not been in previous contact with chlorine. Resulting overall decay coefficients at 20 °C were 24 and 34 d^{-1} respectively, which are considerably lower than uptake rates observed in the October series of experiments. These decay rates include water column decay, which was not explicitly quantified. At the time of the July tests, the North Saskatchewan was experiencing much higher flows than during the October, 1990 experiments. Although no quantitative data is available, the sediment load was also visibly much higher.

The higher flowrates and velocities associated with the July 1991 tests may have been largely responsible for the differences observed between the two benthic sampling periods. At higher discharges, the riverbed is subjected to increased scour, which may have re-suspended a significant portion of the benthal deposits responsible for the chlorine uptake. Krenkel and Novotny (1980) quoted several sources who reported sediment deposition at velocities less than 0.33 m^3/s, and scour and re-suspension of these deposits at stream velocities greater than this value. Removal of much of the bed material present in the October 1990 study may have resulted in the reduced rate of chlorine reaction observed in July.

Benthic deposits have been recognized as a possible sink for organic contaminants and dissolved oxygen. This demand results primarily from activity within the biological community within the benthos that utilize the contaminants as an energy source. Both aerobic and anaerobic bacteria exist within the bottom sediments; the aerobic layer may extend to only a small depth into the sediment. Rates of degradation within the benthos are usually small relative to other processes due to the low rates associated with anaerobic bio-chemical purification processes (Rinaldi et al., 1979). However, chlorine reaction and uptake rates within the benthos may proceed at much greater rates as the dominant reaction mechanism is probably oxidation, not bio-degradation.

A slight difference between the rates observed in the two July tests was seen, with chlorine uptake in the area which had received prior chlorine exposure occurring at a reduced pace. This may indicate that previous exposure to chlorine would result in reduced rates of consumption, possibly as much of the easily oxidizable matter would be consumed with the initial exposure to residual chlorine. If such a sensitivity did exist within the benthos, it may help to explain the wide differences seen between the gross chlorine decay rate within the discharge plume and the benthic uptake rates obtained during the October 1990 experiments. Downstream chlorine residuals were monitored only after the plume had established a steady-state condition. This required greater than 4 hours of continuous discharge, which may have satisfied the initial chlorine demand within the sediment, resulting in a greatly attenuated rate of uptake over the remainder of the test.

Variations observed in the two series of field tests indicate that the rate of benthic chlorine uptake may be highly variable, both spatially and temporally. Although the use of batch experiments such as those used in this study may not adequately simulate the complete physical system, they do provide valuable order-of-magnitude approximations of chlorine uptake kinetics. Unfortunately, no published literature on this subject was found, preventing the comparison of this data to that of other researchers. While the available data provides no conclusive relationship between benthic uptake rates of chlorine and other stream parameters, it does indicate in a qualitative manner that the benthos is a significant sink for residual chlorine within the North Saskatchewan River.

7.2.2.4 Chlorine Volatilization

Although volatilization has been recognized as an important pollutant sink in natural waterbodies, difficulties in determination of parameters governing the rate and extent of volatilization have limited the availability of actual field data. Laboratory studies, in which individual processes are easily controlled and measured are usually used to obtain estimates of pollutant volatility.

The volatility of pollutants is frequently described by the Henry's Law constant (Equation 2.11), which relates the equilibrium partitioning of a substance between the aqueous and liquid phases. The Henry's Law coefficient (H) is based on a relative scale, with substances with H greater than approximately 0.001 considered to be highly volatile (Rathbun, 1990). Reckhow et al. (1990) determined from experimental data a H of 0.0055 atm m^3 mol^{-1} for monochloramine. This would suggest that monochloramine could be considered to be a highly volatile compound, and that loss to the atmosphere would represent a significant sink within a river system. Henry's Law provides a valuable estimate of the relative volatility of a pollutant, but is applicable only to equilibrium conditions.

The rate of transfer of a substance from water to the atmosphere has been the subject of much research. The two-film model , which assumes uniformly mixed water and air phases which are separated by thin films of air and water is commonly used to describe the process of volatilization (Rathbun, 1990, Smith et al., 1980; Matter-Müller et al., 1981). This model assumes that the rates of volatilization are controlled by molecular diffusion through the two films, with the results being additive. For substances of high volatility, transfer is assumed to be liquid phase limiting, whereas for solutes of low volatility, gas-phase diffusion is assumed to be the rate-limiting step. The two-film model has been expressed mathematically (Matter-Müller et al., 1981) as:

$$\frac{1}{K_{OL}} = \frac{1}{k_L} + \frac{RT}{Hk_G} \qquad (7.1)$$

where: K_{OL} = the overall volatilization mass-transfer coefficient (m d^{-1})
k_L = the liquid-film mass-transfer coefficient (m d^{-1})
R = ideal gas constant (kPa m^3 g^{-1} mol^{-1})
T = absolute temperature (°K)
H = Henry's Law constant (kPa m^3 g^{-1} mol^{-1})
and k_G = gas-film mass-transfer coefficient (m d^{-1})

Application of this model requires knowledge of the liquid-film and gas-film transfer coefficients.

For volatile substances, with $H > 0.001$ atm m^3 mol^{-1}, liquid-phase resistance controls the rate of volatilization, and the term $\frac{RT}{Hk_G}$ in Equation 7.1 becomes insignificant (Smith et al., 1980). Few reports of a Henry's Law coefficient for the chlorine species of interest are available within the literature: the rapid rate of decay of most TRC species may prevent the attainment of an equilibrium distribution between the aqueous and gaseous phases, making experimental measurement difficult. However, some values of H have been published, and as they assist in understanding the physical behaviour of the compounds, they will be used in this discussion. Reckhow et al. (1990) reported an experimental value of H = 0.0055 atm m^3 mol^{-1} for combined residual chlorine at 20 °C, and a value of 0.014 atm m^3 mol^{-1} has been reported for molecular chlorine (American Water Works Association, 1990). For Henry's Law coefficients of this magnitude, the rates of volatilization of residual chlorine within the environment would therefore be controlled by diffusion through the liquid.

An estimate of possible rates of volatilization of TRC from the North Saskatchewan River was made according to the method of Rathbun (1990). This analysis was based upon application of the two-film model, with estimates of the gas-film and liquid-film mass transfer coefficients obtained according to the reference-substance concept (Rathbun, 1990). Laboratory measurements of these mass-transfer coefficients exist for only a few solutes, and predictive methods must be used for the many compounds, including monochloramine, for which no laboratory data exists. The liquid-film coefficient for the reference substance is estimated based upon the reaeration coefficient of the stream (K_2), calculated according to the method of O'Connor and Dobbins (Rathbun, 1977) and corrected for the water depth. Rathbun and Tai (1983) presented predictive equations for estimation of the gas-film mass-transfer coefficient for water evaporation as a function of water temperature and wind speed. Reach-averaged values for the river properties obtained during the E.L. Smith field studies were used for all calculations, with a water temperature of 20 °C and no mean winds assumed.

Mass transfer parameters for monochloramine were estimated from those obtained for the reference substances based upon correlations developed by Rathbun (1990). The liquid-film reference substance parameter for chloramine (k_L) was calculated based upon the molal volume of monochloramine at normal boiling temperature, using the Le Bas procedure (Reid et al., 1987). The gas-film transfer coefficient (k_G) for monochloramine was similarly estimated using molecular weight as the correlating parameter. The Henry's Law coefficient for monochloramine was obtained from Reckhow et al. (1990). Using these parameters, the overall mass-transfer coefficient for monochloramine (K_{OL}) could be calculated, using Equation 7.1.

Using the above parameters, downstream predictions of residual chlorine concentrations could be generated. For illustrative purposes, the river is assumed to be completely-mixed, with a monochloramine concentration of 2.0 mg/L. Using reach-averaged hydraulic parameters, monochloramine concentrations at downstream points could be calculated using the equation presented in Rathbun (1990).

$$\frac{C}{C_o} = \exp\left(\frac{-K_{OL}\, t}{Y} \right) \qquad (7.2)$$

This method will predict downstream concentrations profiles, with volatilization assumed to be the only loss mechanism. Results from this analysis, calculated over a distance of 20 km, are shown in Figure 7.3. Volatilization of compounds from streams is considered a first-order process (Rathbun and Tai, 1983: Rathbun and Tai, 1982; Smith et al., 1980), and inspection of the form of Equation 7.2 suggests that a first-order decay coefficient due to volatilization k_v, could be derived as a function of K_{OL} and the mean channel depth Y. Using data from above, a first-order rate coefficient within the North Saskatchewan river for the volatilization of monochloramine of $k_v = 1.82\ d^{-1}$ results.

Based upon the above analysis, reduction in monochloramine due to volatilization proceeds at a relatively slow rate. As can be seen in Figure 7.3, a reduction in TRC concentration of 90% requires a distance of approximately 100 km. Although other total chlorine species will volatilize at differing rates, monochloramine is the dominant species, and Equation 7.2 should approximate the environmental behaviour reasonably well. The field tests

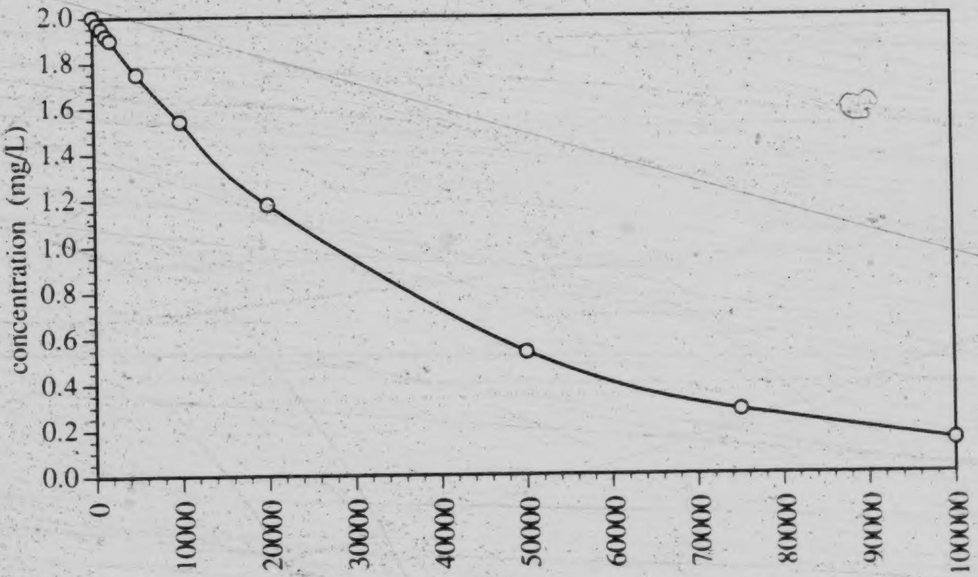


Figure 7.3 Predicted fully-mixed downstream concentrations of TRC in North Saskatchewan River using volatilization model of Rathbun (1990).

conducted in this study found no detectable chlorine at a distance greater than 1400 m downstream from the outfall, a distance over which little volatilization of TRC would be predicted by Equation 7.2 This is further confirmed by comparison of the predicted rate constant with those observed in the field studies, as k_v represents less than 10% of the gross decay rate. This suggests that volatilization may not have contributed significantly to the depletion of TRC within the North Saskatchewan River.

The results of this study, which suggest that volatilization may not be the predominant decay mechanism contrast with the results of Reckhow et al. (1990), the only other known field study where an assessment of the decay pathways was attempted. They concluded that volatilization was the predominant mechanism for the reduction of residual chlorine concentrations in Lampson Brook, Massachusetts, accounting for more than 50% of the lost chlorine. Chemical demand and photosynthesis accounted for very minor decay. They did not account for benthic chlorine demand, which was indirectly incorporated into the volatilization term. The results of the benthic tests conducted in this study suggest that this may have neglected a significant chlorine sink, and the decay attributed to volatilization may have included a substantial benthic demand. Lampson Brook is also a small stream relative to the North Saskatchewan River, with a mean channel depth of less than 0.25 m. As the rate of volatilization varies inversely with the channel depth (Reckhow et al., 1990; Rathbun, 1990; Abdel-Gawad and Bewtra, 1988), the relative contribution of volatilization may have been higher.

8.0 Summary and Conclusions

Field investigations of the decay of residual chlorine from discharges at the City of Edmonton's Rossdale and E.L. Smith Water Treatment Plants were conducted downstream from these treatment plants. These investigations consisted of Rhodamine WT tracer studies, to provide information on the mixing characteristics of the North Saskatchewan River, and studies of the downstream distribution of TRC resulting from a steady-state discharge of chlorinated waters. As the North Saskatchewan River is a relatively large river, it was not accurate to assume complete mixing of the effluent within the river. The site-specific hydraulic behaviour of the plume was predicted using the numerical mixing model TRSMIX. The rate of chlorine decay within the receiving water body was also determined using TRSMIX.

Information obtained from the field investigations were supplemented with additional data gathered from bench-scale laboratory and field investigations. This information provided information on the fate of residual chlorine within the receiving environment, and indicated the most important mechanisms for chlorine decay. The results of this study are summarized as:

(1) The decay of total residual chlorine within the North Saskatchewan River was found to follow first-order kinetics. Decay rates of 20 d^{-1} and 28 d^{-1} (at 20 °C) were observed downstream from the E.L. Smith and Rossdale Water Treatment Plants respectively. A lower-bound on the decay rate was observed to be 13 d^{-1} and 11 d^{-1} respectively. Decay rates seen in this study compare well with the few reported values obtained from other field investigations. However, they are higher than those generally reported from laboratory investigations, indicating the utility of site-specific assessment.

(2) Photolytic decomposition does not appear to be an important mechanism for the removal of residual chlorine within the North Saskatchewan River. No significant difference (at a 95% level of significance) between day-time and night-time samples was observed in samples collected from the E.L. Smith chlorine plume.

(3) Chlorine decomposition and reaction with chemical constituents present in the water column represented approximately 10 to 20 % of the overall rate of chlorine decay at the time of the plume studies.

(4) Loss of chlorine from the receiving water body to the atmosphere through volatilization was not explicitly measured. However, predictions of the rates of TRC volatilization using theoretically based modelling techniques suggests that volatilization losses in the North Saskatchewan River may have represented 5 to 10 % of the gross rate of decay.

(5) A significant demand for chlorine appears to exist within the benthic layer, and this sink may have been overlooked in previous studies. Rates of TRC uptake obtained from in-situ batch experiments consistently yielded first-order decay rates faster than the overall rate of decay seen in the plume study. Due to limited data, it was not possible to relate the rate of benthic chlorine uptake to the overall rate of chlorine decay within the North Saskatchewan. The rates were observed to vary over two orders of magnitude, and may be heavily dependent upon site-specific and variable conditions. Uncertainty exists as to whether this represents a relatively constant demand, or one that decreases with prior chlorine exposure.

9.0 Recommendations for Future Work

Several areas where additional knowledge of chlorine behaviour within the receiving environment would be useful have been identified. These are as follows:

(1) Additional field work should be conducted to increase the available database on the decay rates of chlorinated water treatment plant effluents within freshwaters. The influence of changing receiving water qualities and streamflow conditions should be determined.

Due to the rapid decay of residual chlorine, a detailed understanding of the hydraulic behaviour of the discharge plume within the receiving stream would be necessary in subsequent field studies. Considerable attention should be directed towards obtaining accurate measurements of velocity profiles and cross-sectional geometry. The requirement that several closely-spaced cross sections be established, and large variations in pollutant concentrations be modelled over a small proportion of the river flow may justify the use of a more-sophisticated finite-element model.

(2) The effect of an ice-cover on the rate of chlorine decay should be determined.

(3) As it is known to be an important mechanism for chlorine decay in the laboratory environment, photo-decomposition of TRC should be investigated further to determine the effects of stream turbidity and other parameters on its relevance to field situations.

(4) Additional study on the relative impact of benthic chlorine demand on the overall rate of chlorine decay should be performed.

(5) Variations in the rates of the above-mentioned processes between free and combined chlorine species should be determined.

(6) Important chemical properties of chlorine and chloramine species that govern their environmental behaviour should be determined. This includes such parameters as Henry's Law coefficients, gas-film and liquid-film mass transfer coefficients, and soil / sediment adsorption coefficients.

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Appendix A

Cross-sectional geometry and flow distribution plots

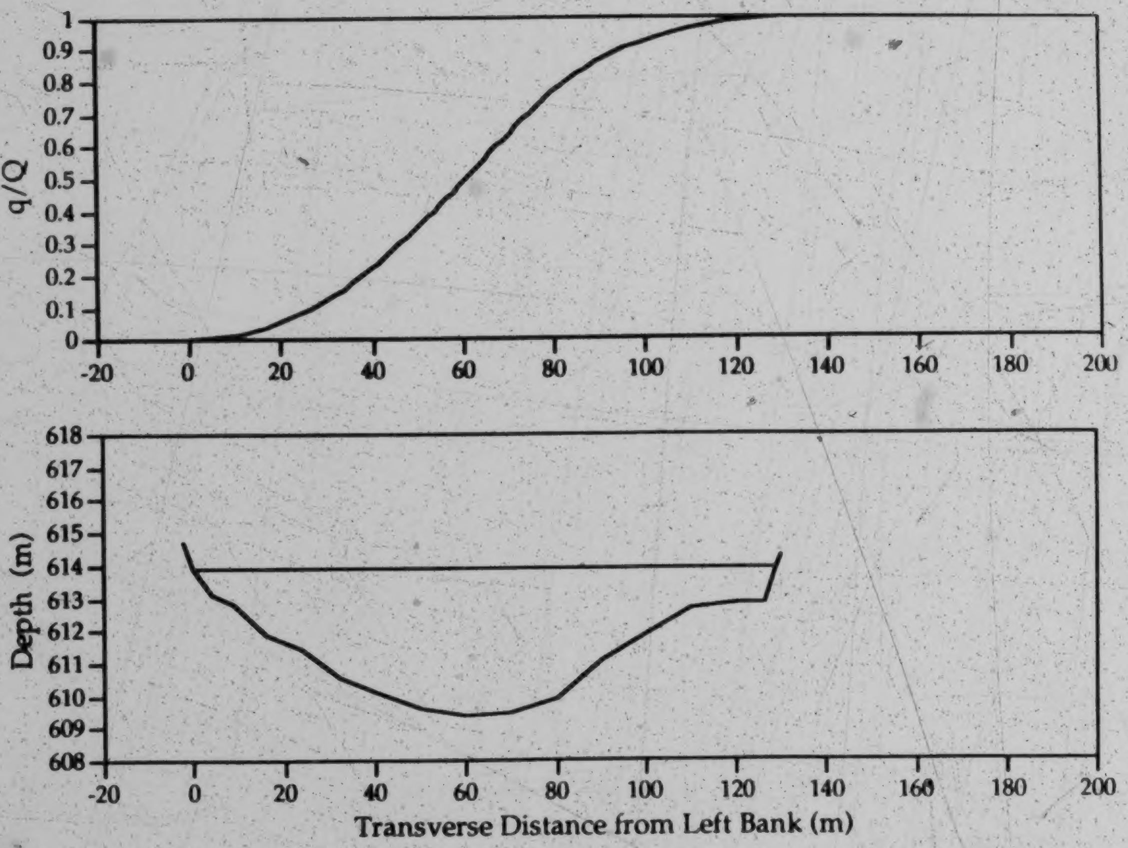

Figure A1 Cross sectional geometry and flow distribution: Rossdale cross section 1.

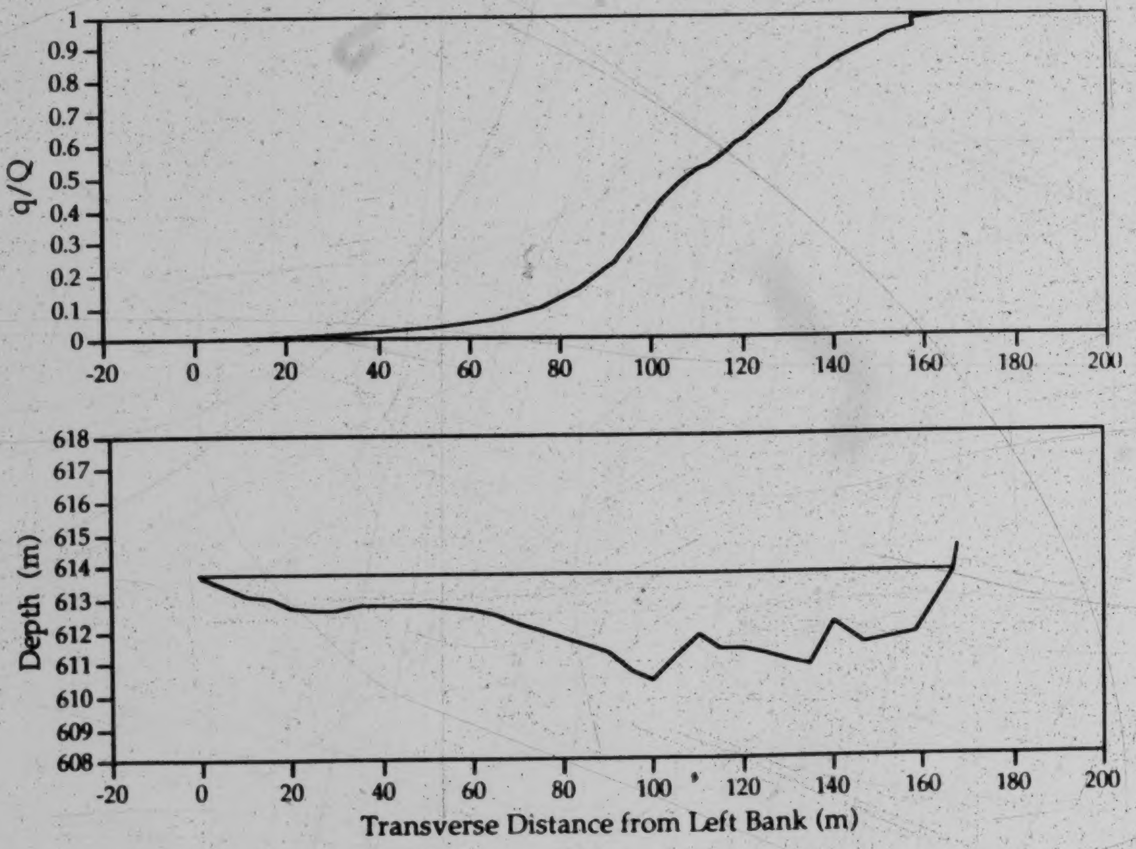

Figure A2 Cross sectional geometry and flow distribution: Rossdale cross section 2.

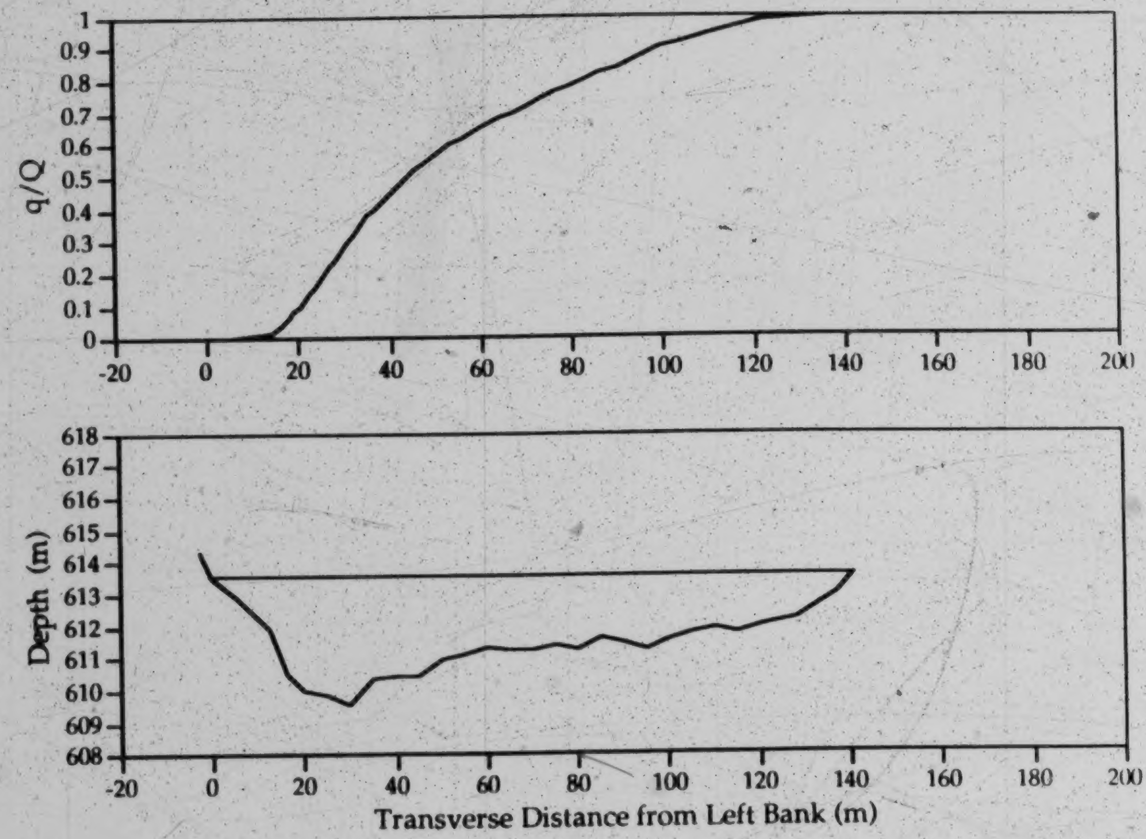

Figure A3 Cross sectional geometry and flow distribution: Rossdale cross section 3.

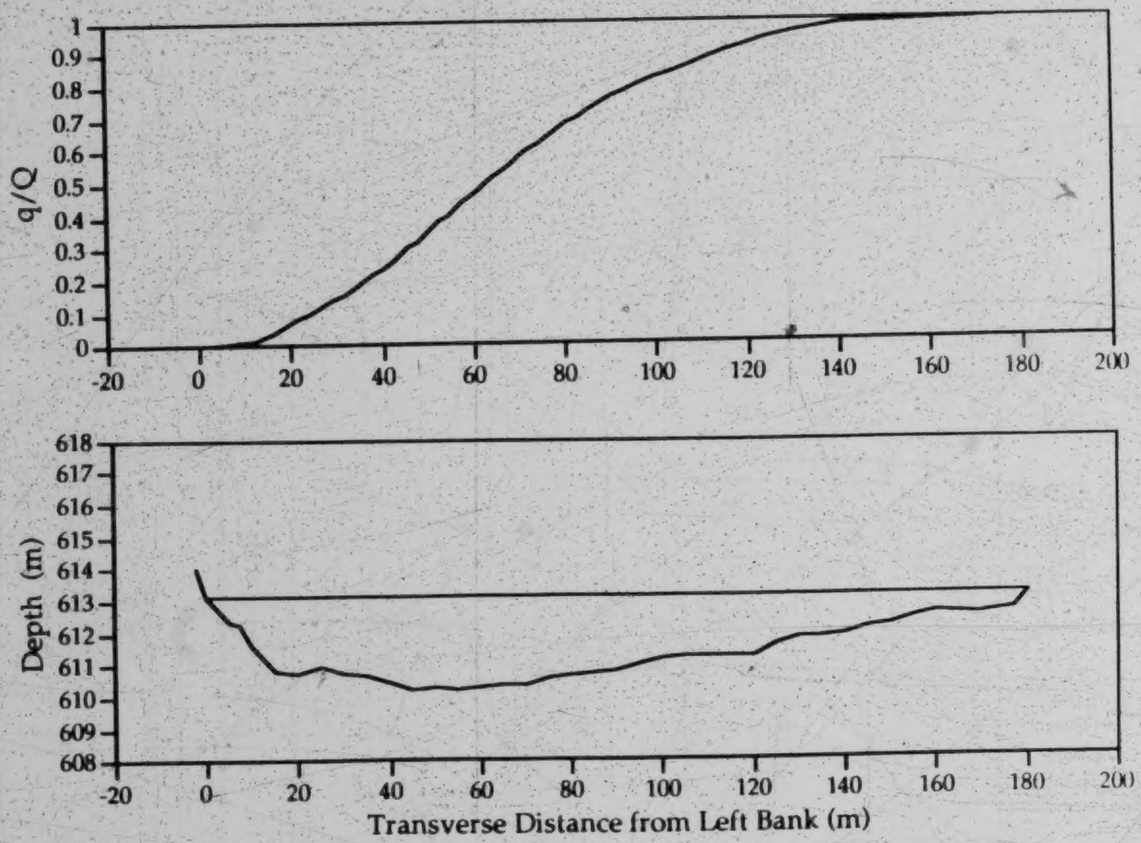

Figure A4 Cross sectional geometry and flow distribution: Rossdale cross section 4.

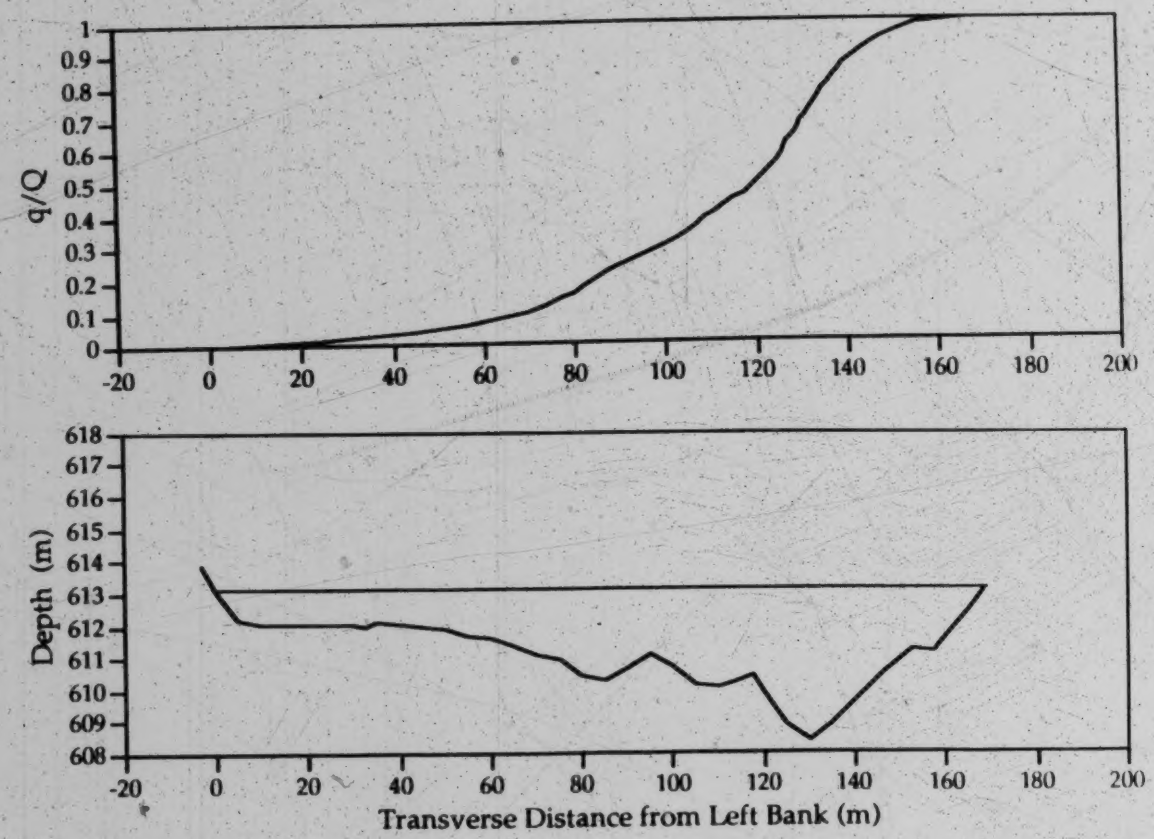

Figure A5 Cross sectional geometry and flow distribution: Rossdale cross section 5.

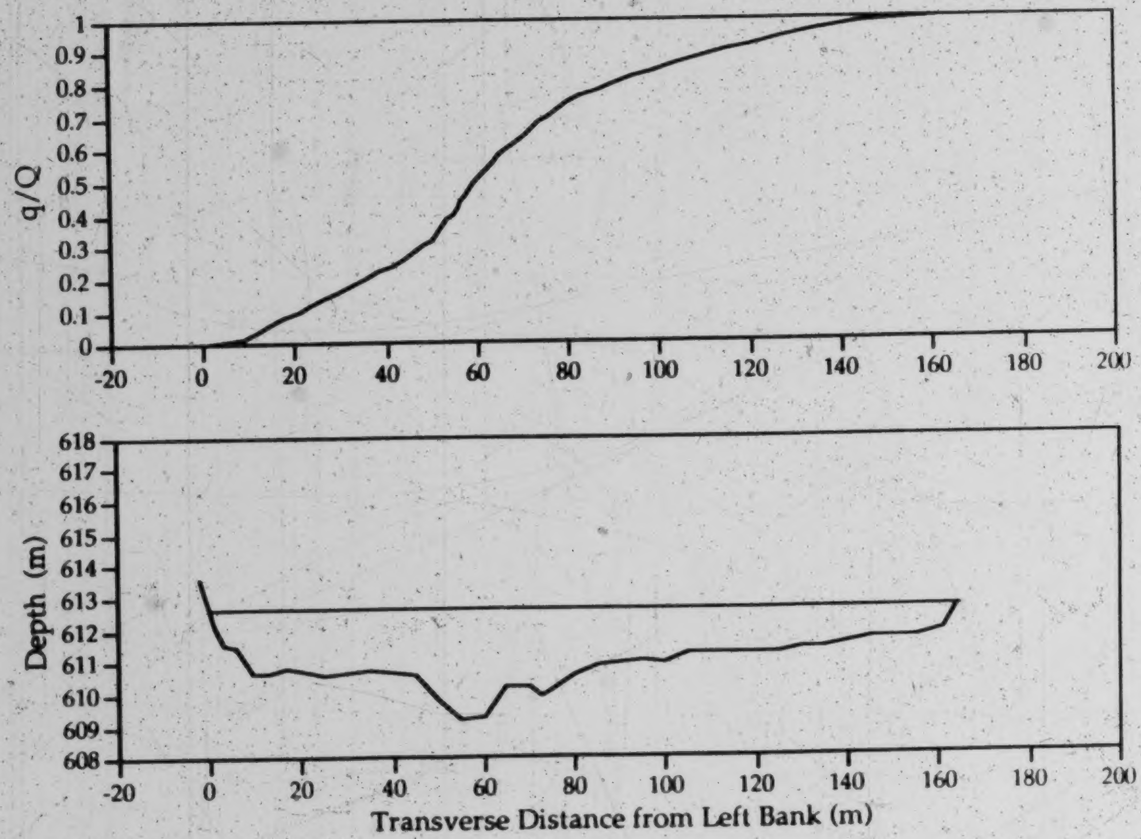

Figure A6 Cross sectional geometry and flow distribution: Rossdale cross section 6.

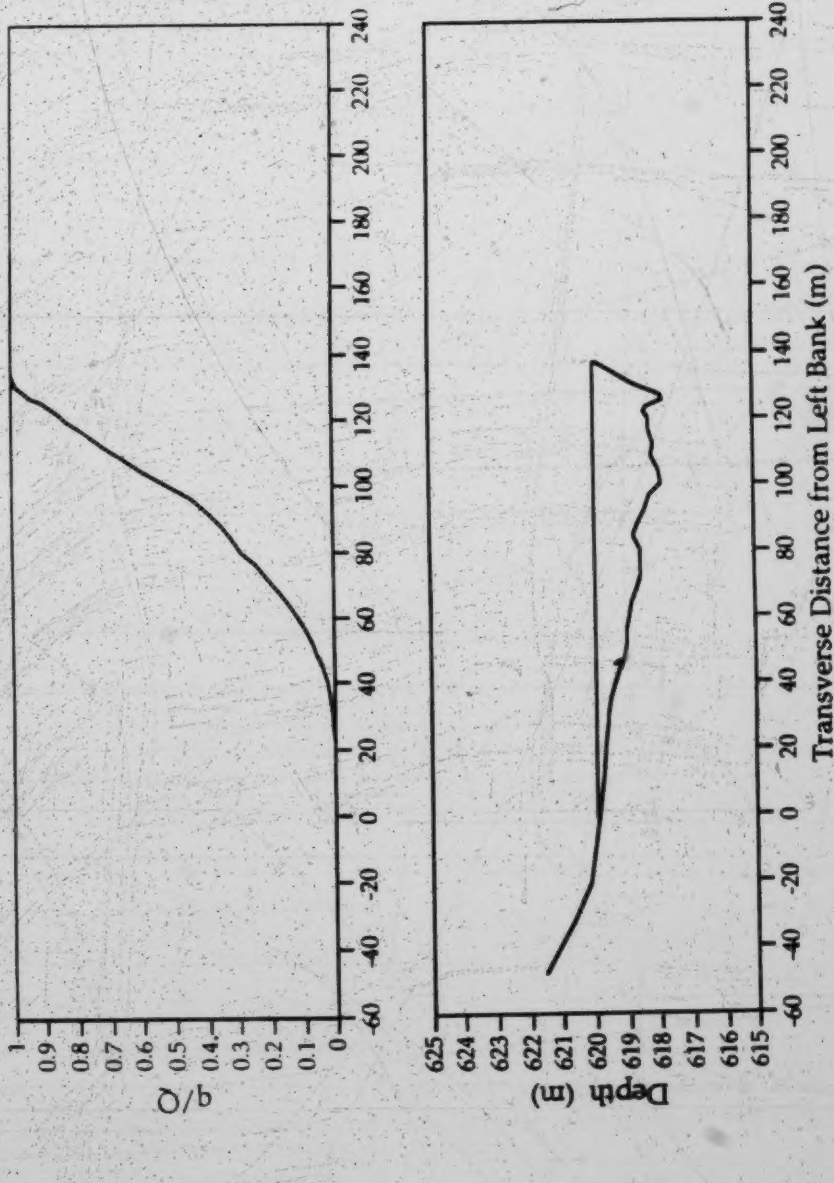

Figure A7 Cross sectional geometry and flow distribution: E.L. Smith cross section 1.

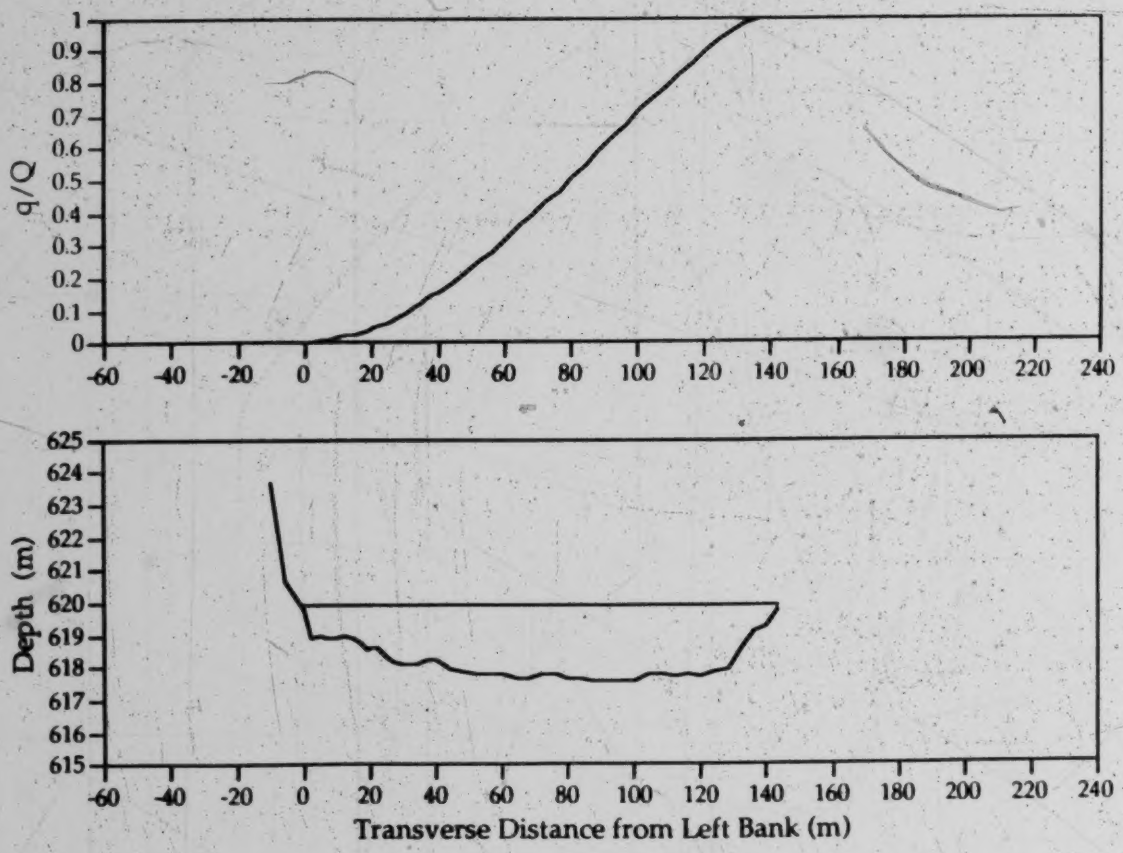

Figure A8 Cross sectional geometry and flow distribution: E.L. Smith cross section 2.

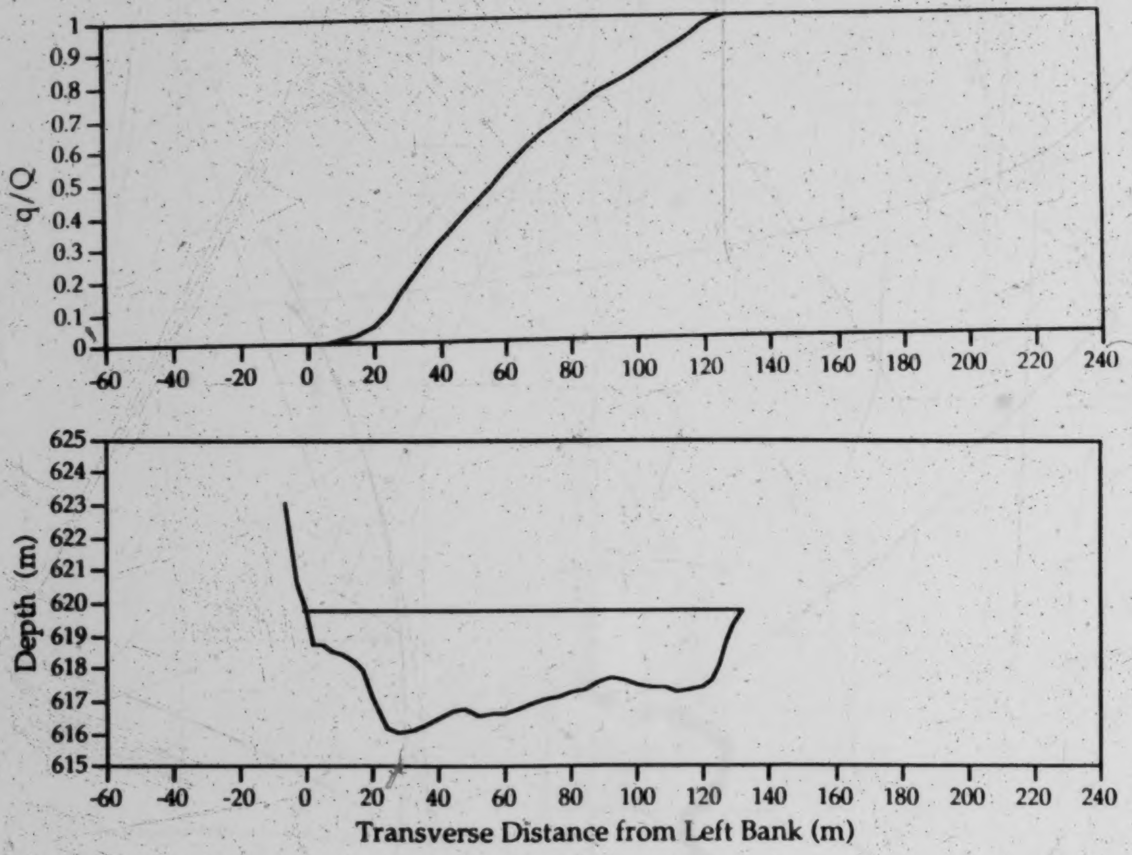

Figure A9 Cross sectional geometry and flow distribution: E.L. Smith cross section 3.

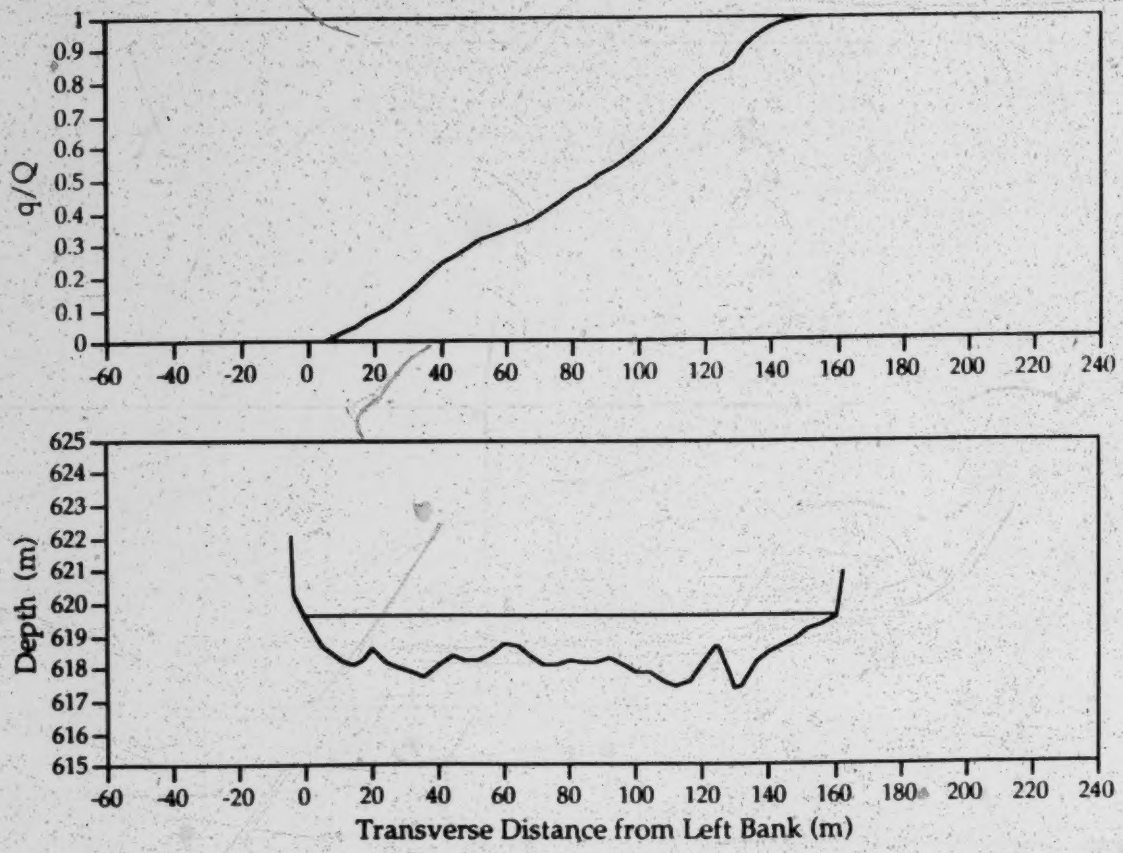

Figure A10 Cross sectional geometry and flow distribution: E.L. Smith cross section 4.

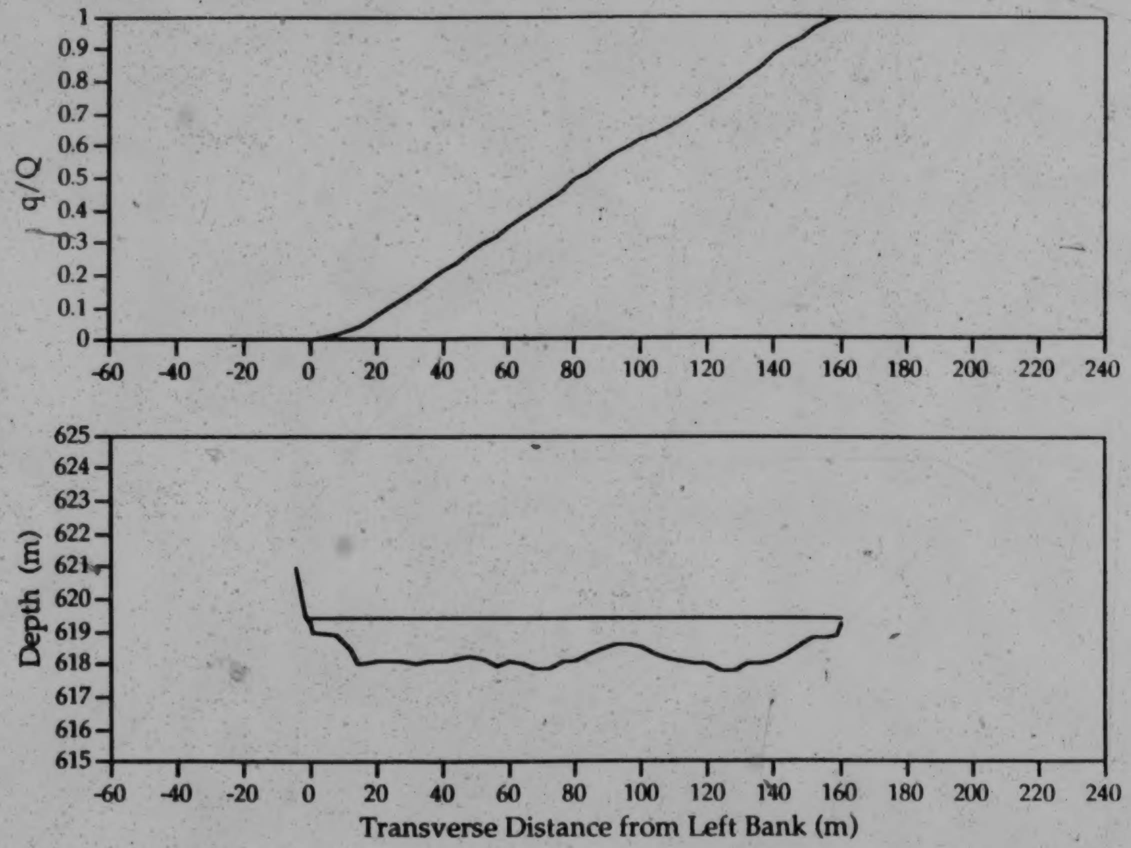

Figure A11 Cross sectional geometry and flow distribution: E.L. Smith cross section 5.

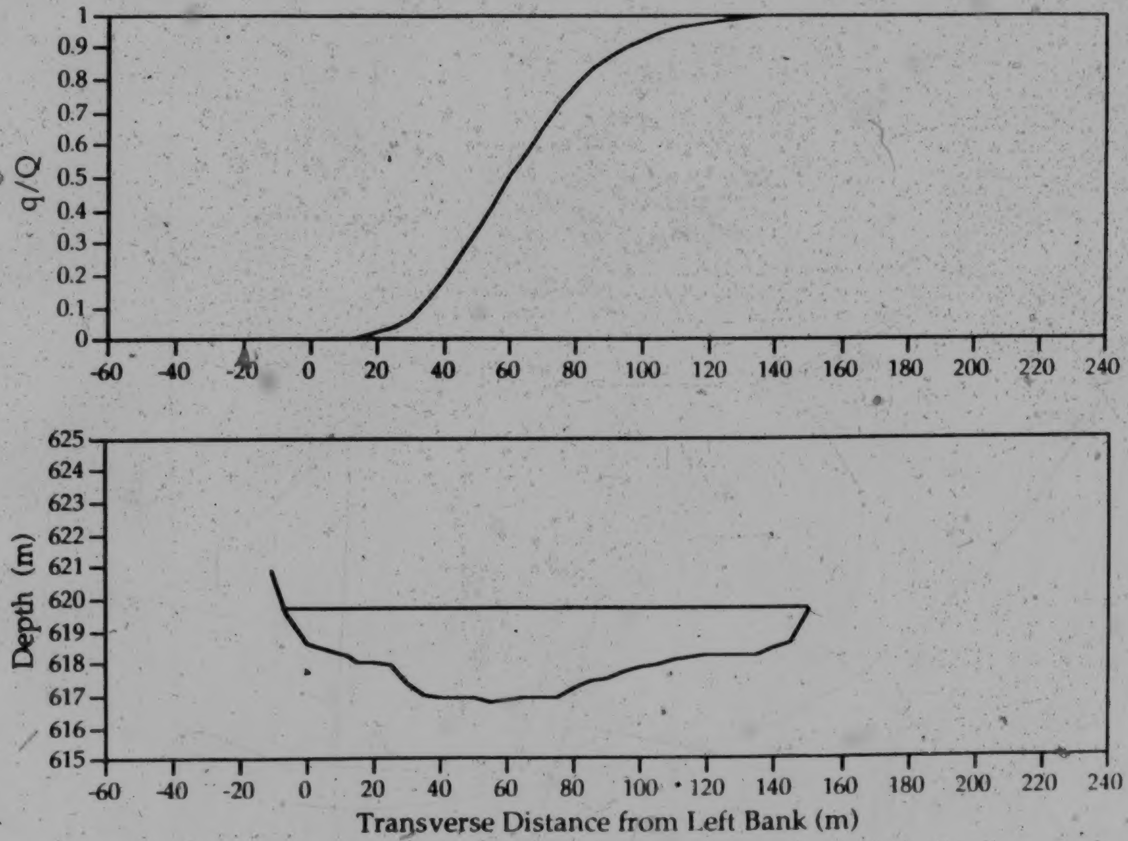

Figure A12 Cross sectional geometry and flow distribution: E.L. Smith cross section 6.

Appendix B

Rhodamine WT tracer study permit

Alberta
ENVIRONMENT
Environmental Protection Services
Standards and Approvals Division

9820 - 106 Street, Edmonton, Alberta, Canada T5K 2L6 403/427-5883 / Fax 403/422-4192

September 4, 1990

Department of Civil Engineering
University of Alberta
EDMONTON, Alberta
T6G 2G7

Attention: Daniel W. Smith

Dear Sir:

RE: Project: Conduct Tracer-Dye Studies in the North Saskachewan River from the Rossdale Water Treatment Plant to the Gold Bar Sewage Treatment Plant
Application No. 90-SA-629

Please find enclosed Letter of Permission No. 90-LP-016, issued under the Clean Water Act. We would urge you to note and comply with the attached terms, conditions and requirements as applied to your operation.

Yours truly,

for J. C. Lack, P. Eng.
Director
Standards and Approvals Division

Enclosures

cc: Pollution Control Division
Alberta Economic Development & Trade
Small Business Development Division
Local Health Unit

Alberta
ENVIRONMENT

LETTER OF PERMISSION

PERMISSION NO. 90-LP-016

FILE NO. 90-SA-629

WHEREAS

Department of Civil Engineering
University of Alberta
EDMONTON, Alberta T6G 2G7

has, pursuant to section 11 of the Clean Water (General) Regulations applied to the Director of Standards and Approvals for permission to

conduct tracer-dye studies in the North Saskatchewan River from the Rossdale Water Treatment Plant to the Gold Bar sewage Treatment plant.

NOW THEREFORE

this permission is issued subject to the terms and conditions and requirements attached hereto.

Edmonton September 04 1990

Director of Standards and Approvals

PERMISSION NO

90-LP-016

TERMS, CONDITIONS AND REQUIREMENTS ATTACHED TO LETTER OF PERMISSION

SECTION ONE: DEFINITIONS

1.1 In this Letter of Permission

(a) "guidelines" means the publication "Measurement of time-of-travel and dispersion in streams by dye tracing: Techniques of Water Resources Investigations, Book 3, Chapter A9, USGS., TW13-A9" by Hubbard et al., 1982;

(b) "point of complete mixing" means the distance downstream of the point of dye injection required for complete lateral mixing of the dye as estimated by equation (1) or (2), whichever is appropriate of the guidelines; and

(c) "test reaches" means the following reaches of the North Saskatchewan River; from the Rossdale Water Treatment Plant to the Gold Bar Sewage Treatment Plant.

SECTION TWO: GENERAL

2.1 The tracer-dye studies shall be carried out under the continuous supervision of the personnel of the Department of Civil Engineering.

2.2 Only Rhodamine WT dye shall be used as the tracer dye.

2.3 The injection of the dye shall be at least 10 centimetres below the free-flowing surface of the river and within the central 75% of the flow.

2.4 The concentration of the tracer dye in the test reaches shall not exceed 10 micrograms per litre

(a) at any withdrawal points for human or industrial usage, or
(b) at any withdrawal points for livestock watering, or
(c) after the point of complete mixing.

2.5 The Department of Civil Engineering shall inform all licenced water withdrawal users in the test reaches, at least 48 hours prior to the commencement of the tracer-dye studies, of:

(a) the purpose of the studies;

(b) the date on which the studies will be conducted; and

(c) what precautions have or will be taken during the period of injection and sampling to ensure the protection of downstream water supplies.

PERMISSION NO

90-LP-016

TERMS, CONDITIONS AND REQUIREMENTS ATTACHED TO LETTER OF PERMISSION

SECTION THREE: REPORTING

3.1 The Director of Standards and Approvals shall be notified at least 24 hours in advance of any tests conducted.

3.2 The notification to the Director of Standards and Approvals shall include the following:

(a) the location of each injection site,
(b) the quantity of dye to be injected at each site,
(c) the terms of injection,
(d) the means of injection,
(e) the location of each sampling site, and
(f) a sampling schedule at each sampling site giving the starting time, the sampling frequencies, and the completion time.

3.3 A report on the tracer-dye studies conducted under this Letter of Permission shall be submitted to the Director of Standards and Approvals, with a copy to the River Engineering Branch of Alberta Environment, prior to January 1, 1990. The report shall include, but not be limited to, a description of the procedures used for injection of the dye, the sampling of the dye, the hydraulic conditions in the test reaches during the period of injection and sampling, and all the raw data collected.

3.4 In the event a test is cancelled, the Department of Civil Engineering shall, at the earliest opportunity, inform all licenced water-withdrawal users and the Director of Standards and Approvals, using the most immediate form of communication, of the cancellation, of any changes that will be made in the test schedule as a result of the cancellation.

SECTION FOUR: EFFECTIVE DATE OF THE LETTER OF PERMISSION

4.1 This Letter of Permission shall become effective upon the date of issue.

SECTION FIVE: EXPIRY DATE OF THE LETTER OF PERMISSION

5.1 This Letter of Permission shall expire on September 30, 1990.

DATED September 4, 1990

J.C. LACK, DIRECTOR

Alberta
ENVIRONMENT
Environmental Protection Services
Standards and Approvals Division

9820 - 106 Street, Edmonton, Alberta, Canada T5K 2L6 403/427-5883 Fax 403/422-4192

September 18, 1990

Department of Civil Engineering
University of Alberta
EDMONTON, Alberta
T6G 2G7

Attention: Dr. Daniel W. Smith

Dear Sir:

RE: Project: Conduct Tracer-Dye Studies in the North Saskatchewan River from the E.L. Smith Water Treatment Plant to the Rossdale Water Treatment Plant
Application No. 90-SA-658

Please find enclosed Letter of Permission No. 90-LP-017, issued under the Clean Water Act. We would urge you to note and comply with the attached terms, conditions and requirements as applied to your operation.

Yours truly,

J. C. Lack, P. Eng.
Director
Standards and Approvals Division

Enclosures

cc: Pollution Control Division
Alberta Economic Development & Trade
Small Business Development Division
Local Health Unit

Alberta
ENVIRONMENT

LETTER OF PERMISSION

PERMISSION NO. 90-LP-017

FILE NO. 90-SA-658

WHEREAS

University of Alberta
Department of Civil Engineering
EDMONTON, Alberta T6G 2G7

has, pursuant to section 11 of the Clean Water (General) Regulations applied to the Director of Standards and Approvals for permission to

conduct tracer-dye studies in the North Saskatchewan River from the E.L. Smith Water Treatment Plant to the Rossdale Water Treatment Plant.

NOW THEREFORE

this permission is issued subject to the terms and conditions and requirements attached hereto.

Edmonton September 18 19 90

Director of Standards and Approvals

PERMISSION NO

90-LP-017

TERMS, CONDITIONS AND REQUIREMENTS ATTACHED TO LETTER OF PERMISSION

SECTION ONE: DEFINITIONS

1.1 In this Letter of Permission

(a) "guidelines" means the publication "Measurement of time-of-travel and dispersion in streams by dye tracing: Techniques of Water Resources Investigations, Book 3, Chapter A9, USGS., TW13-A9" by Hubbard et al., 1982;

(b) "point of complete mixing" means the distance downstream of the point of dye injection required for complete lateral mixing of the dye as estimated by equation (1) or (2), whichever is appropriate of the guidelines; and

(c) "test reaches" means the following reaches of the North Saskatchewan River; from the E.L. Smith Water Treatment Plant to the Rossdale Water Treatment Plant.

SECTION TWO: GENERAL

2.1 The tracer-dye studies shall be carried out under the continuous supervision of the personnel of the Department of Civil Engineering.

2.2 Only Rhodamine WT dye shall be used as the tracer dye.

2.3 The injection of the dye shall be at least 10 centimetres below the free-flowing surface of the river and within the central 75% of the flow.

2.4 The concentration of the tracer dye in the test reaches shall not exceed 10 micrograms per litre

(a) at any withdrawal points for human or industrial usage, or
(b) at any withdrawal points for livestock watering, or
(c) after the point of complete mixing.

2.5 The Department of Civil Engineering shall inform all licenced water withdrawal users in the test reaches, at least 48 hours prior to the commencement of the tracer-dye studies, of:

(a) the purpose of the studies;

(b) the date on which the studies will be conducted; and

(c) what precautions have or will be taken during the period of injection and sampling to ensure the protection of downstream water supplies.

PERMISSION NO

90-LP-017

TERMS, CONDITIONS AND REQUIREMENTS ATTACHED TO LETTER OF PERMISSION

SECTION THREE: REPORTING

3.1 The Director of Standards and Approvals shall be notified at least 24 hours in advance of any tests conducted.

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(a) the location of each injection site,
(b) the quantity of dye to be injected at each site,
(c) the terms of injection,
(d) the means of injection,
(e) the location of each sampling site, and
(f) a sampling schedule at each sampling site giving the starting time, the sampling frequencies, and the completion time.

3.3 A report on the tracer-dye studies conducted under this Letter of Permission shall be submitted to the Director of Standards and Approvals, with a copy to the River Engineering Branch of Alberta Environment, prior to January 1, 1990. The report shall include, but not be limited to, a description of the procedures used for injection of the dye, the sampling of the dye, the hydraulic conditions in the test reaches during the period of injection and sampling, and all the raw data collected.

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SECTION FOUR: EFFECTIVE DATE OF THE LETTER OF PERMISSION

4.1 This Letter of Permission shall become effective upon the date of issue.

SECTION FIVE: EXPIRY DATE OF THE LETTER OF PERMISSION

5.1 This Letter of Permission shall expire on September 30, 1990.

DATED September 18, 1990

J.C. LACK, DIRECTOR

Appendix C

Rhodamine WT tracer data

Table C1. Rhodamine WT tracer data from Rossdale field tests

Cross-section	Transverse distance (m)	Mean Concentration † (µg/L)	Standard Deviation	Coefficient of Variation (%)
1	2.0	40.785	1.488	3.6
1	3.0	24.451	1.432	5.9
1	4.5	18.760	5.380	28.7
1	6.5	5.941	1.709	28.8
1	10.0	1.366	0.504	36.9
1	18.0	0.005	0.009	164.2
2	2.5	7.434	0.269	3.6
2	4.5	7.119	0.264	3.7
2	8.0	5.206	0.147	2.8
2	12.0	4.854	0.535	11.0
2	16.0	2.970	0.168	5.7
2	20.0	0.891	0.095	10.7
2	28.0	ldl	0.002	not reported
3	3.0	3.263	0.174	5.3
3	8.0	1.728	0.760	44.0
3	12.0	0.576	0.193	33.4
3	18.0	0.023	0.022	94.5
3	24.0	ldl	0.002	not reported
3	30.0	ldl	0.003	not reported
3	40.0	ldl	0.001	not reported
4	3.0	0.332	0.002	0.5
4	6.0	0.318	0.004	1.1
4	11.0	0.282	0.021	7.4
4	16.0	0.268	0.005	1.9
4	24.0	0.208	0.004	1.9
4	32.0	0.175	0.006	3.7
4	40.0	0.144	0.001	0.5
4	50.0	0.105	0.034	32.5
5	3.0	0.335	0.011	3.4
5	6.0	0.299	0.006	1.9
5	10.0	0.297	0.028	9.4
5	16.0	0.258	0.006	2.2
5	24.0	0.211	0.008	3.6
5	32.0	0.219	0.002	0.9
5	40.0	0.194	0.006	3.0
5	50.0	0.196	0.003	1.6
5	60.0	0.186	0.009	4.9
5	75.0	0.162	0.008	5.1
6	3.0	0.136	0.003	2.3
6	6.0	0.139	0.002	1.4
6	10.0	0.136	0.003	2.4
6	16.0	0.132	0.007	5.3
6	24.0	0.117	0.000	0.3
6	32.0	0.108	0.005	4.8
6	40.0	0.114	0.026	22.6
6	50.0	0.082	0.002	2.2
6	60.0	0.072	0.003	3.6
6	75.0	0.058	0.007	12.4

† ldl - less than detection limit

Table C2. Rhodamine WT tracer data from E.L. Smith field tests

Cross-section	Transverse distance (m)	Mean Concentration † (µg/L)	Standard Deviation	Coefficient of Variation (%)
6	3.0	0.219	0.004	1.8
6	6.0	0.232	0.003	1.4
6	9.0	0.248	0.005	2.0
6	12.0	0.259	0.006	2.4
6	18.0	0.287	0.027	9.4
6	24.0	0.313	0.052	16.5
6	30.0	0.156	0.020	13.1
6	40.0	0.025	0.028	111.2
6	50.0	ldl	0.005	not reported
6	60.0	ldl	0.001	not reported
6	80.0	ldl	0.001	not reported
5	3.0	0.534	0.009	1.6
5	6.0	0.537	0.010	1.8
5	9.0	0.521	0.010	2.0
5	12.0	0.505	0.006	1.2
5	16.0	0.454	0.012	2.6
5	20.0	0.375	0.015	4.1
5	24.0	0.300	0.008	2.7
5	30.0	0.209	0.011	5.4
5	40.0	0.098	0.010	9.7
5	50.0	0.010	0.029	306.3
4	3.0	0.726	0.009	1.3
4	6.0	0.705	0.014	2.0
4	9.0	0.732	0.030	4.1
4	12.0	0.664	0.045	6.7
4	16.0	0.492	0.006	1.3
4	20.0	0.413	0.015	3.5
4	24.0	0.340	0.028	8.2
4	30.0	0.130	0.079	61.3
4	40.0	0.075	0.006	8.3
3	3.0	2.023	0.023	1.1
3	6.0	2.055	0.018	0.9
3	9.0	1.725	0.016	0.9
3	12.0	1.637	0.023	1.4
3	16.0	1.584	0.247	15.6
3	20.0	0.690	0.121	17.6
3	24.0	0.468	0.125	26.7
3	30.0	0.118	0.063	53.2
2	3.0	20.142	0.532	2.6
2	6.0	15.848	8.107	51.2
2	9.0	17.163	0.641	3.7
2	12.0	2.621	0.058	2.2
2	15.0	0.187	0.017	9.2
2	18.0	ldl	0.001	not reported
2	21.0	ldl	0.002	not reported
2	24.0	ldl	0.001	not reported

† ldl - less than detection limit

Table C2 con't

Cross-section	Transverse distance (m)	Mean Concentration † (µg/L)	Standard Deviation	Coefficient of Variation (%)
1	3.0	ldl	not reported	not reported
1	5.0	4.649	2.147	46.2
1	6.0	36.442	3.267	9.0
1	7.0	90.323	5.025	5.6
1	8.0	94.080	1.868	2.0
1	9.0	80.891	3.341	4.1
1	10.0	10.075	0.268	2.7
1	11.0	0.144	0.082	56.9
1	12.0	ldl	0.004	not reported
1	15.0	ldl	0.001	not reported

† ldl - less than detection limit

Appendix D

Fluorometer calibration plot

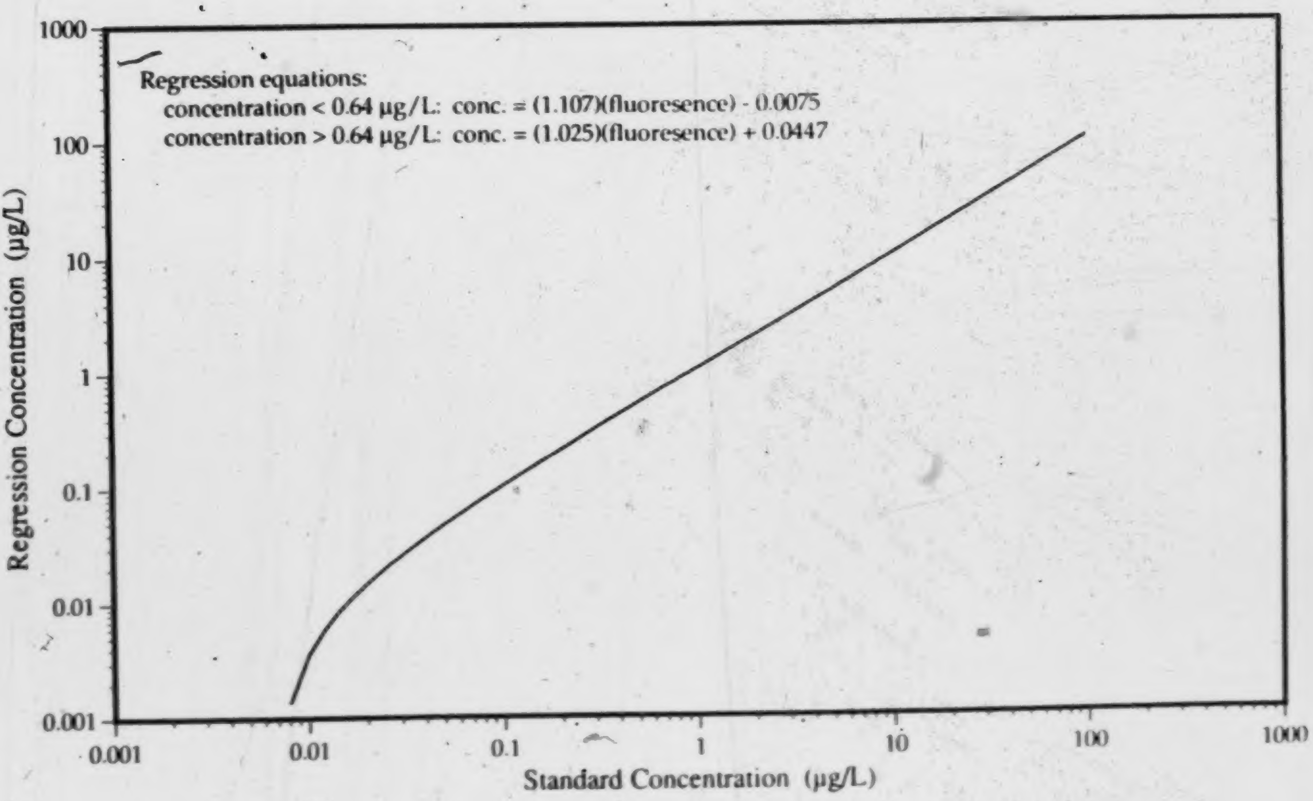

Figure D1 Fluorometer calibration plot

Appendix E

Residual chlorine data

Table E1 Chlorine residual data from Rossdale plume.

Cross Section	Transverse Distance (m)	Replicate	TRC † (mg/L as Cl2)	mean TRC concentration (mg/L as Cl2)	standard deviation (mg/L)	coefficient of variation (%)
1	2.5	1	0.465			
1	2.5	2	0.479			
1	2.5	3	0.487	0.477	0.011	2.3
1	5	1	0.665			
1	5	2	0.975	0.820	0.219	26.8
1	5	3	-			
1	5.5	1	0.186			
1	5.5	2	0.355	0.270	0.119	44.0
1	5.5	3	-			
1	8	1	0.275			
1	8	2	0.275	0.275	0.000	0.0
1	8	3	-			
1	11	1	0.222			
1	11	2	0.177			
1	11	3	0.204	0.201	0.022	11.1
1	14	1	ldl			
1A	3	1	0.292			
1A	3	2	0.190	0.241	0.073	30.2
1A	3	3	-			
1A	6	1	0.138			
1A	6	2	0.160			
1A	6	3	0.159	0.153	0.012	8.1
1A	12	1	0.063			
1A	12	2	0.058			
1A	12	3	0.059	0.060	0.003	4.5
1A	18	1	0.007			
1A	18	2	0.021			
1A	18	3	0.015	0.014	0.007	50.7
2	2.5	1	0.019			
2	2.5	2	0.109			
2	2.5	3	0.157			
2	2.5	4	0.162	0.112	0.066	59.2
2	5	1	0.164			
2	5	2	0.166			
2	5	3	0.170	0.167	0.003	1.7
2	10	1	0.151			
2	10	2	0.100			
2	10	3	0.148	0.133	0.029	21.7
2	15	1	0.080			
2	15	2	0.089			
2	15	3	0.083	0.084	0.004	5.4
2	20	1	0.033			
2	20	2	0.022			
2	20	3	0.031	0.029	0.006	20.4
2	25	1	0.013			
2	25	2	0.013			
2	25	3	0.014	0.013	0.001	5.0
3	3	1	0.066			
3	3	2	0.029			
3	3	3	0.047	0.047	0.019	39.3
3	6	1	0.052			
3	6	2	0.054			
3	6	3	0.053	0.053	0.001	1.7

Table E1 con't

Cross Section	Transverse Distance (m)	Replicate	TRC † (mg/L as Cl2)	mean TRC concentration (mg/L as Cl2)	standard deviation (mg/L)	coefficient of variation (%)
3	9	1	0.074			
3	9	2	0.052			
3	9	3	0.067	0.065	0.012	17.9
3	12	1	ldl			
3	12	2	ldl			
3	12	3	0.013	0.013		
3	18	1	ldl			
3	18	2	ldl	ldl		
3	18	3	-			
3	32	1	ldl			
3	32	2	ldl	ldl		
3	32	3	-			
4	1	1	ldl	ldl		
4	4	1	ldl			
4	4	2	ldl	ldl		

† ldl - less than detection limit

Table E2 Chlorine residual data from E.L. Smith plume.

Cross Section	Transverse Distance (m)	Replicate	TRC † (mg/L as Cl2)	mean TRC concentration (mg/L as Cl2)	standard deviation (mg/L)	coefficient of variation (%)
1	3	1	1.728			
1	3	2	1.728			
1	3	3	1.883	1.780	0.090	5.0
1	6	1	2.083			
1	6	2	2.016			
1	6	3	2.038	2.046	0.034	1.7
1	9	1	2.083			
1	9	2	1.728			
1	9	3	2.016	1.942	0.188	9.7
1	12	1	2.127			
1	12	2	2.083			
1	12	3	2.127	2.112	0.026	1.2
1	15	1	1.905			
1	15	2	1.905			
1	15	3	1.928	1.913	0.013	0.7
1	18	1	1.086			
1	18	2	1.064			
1	18	3	1.019	1.056	0.034	3.2
1	21	1	0.111			
1	21	2	0.133			
1	21	3	0.133	0.126	0.013	10.2
1	24	1	ldl			
1	24	2	ldl			
1	24	3	ldl			
2	3	1	1.174			
2	3	2	1.219			
2	3	3	1.086	1.160	0.068	5.8
2	6	1	1.130			
2	6	2	1.219			
2	6	3	1.285	1.211	0.078	6.4
2	9	1	1.285			
2	9	2	1.307			
2	9	3	1.329	1.307	0.022	1.7
2	12	1	0.532			
2	12	2	0.443	0.487	0.063	12.9
2	12	3	-			
2	15	1	0.133			
2	15	2	0.133			
2	15	3	0.142	0.136	0.005	3.8
2	18	1	0.066			
2	18	2	0.035			
2	18	3	0.035	0.046	0.018	39.1

Table E2 con't

Cross Section	Transverse Distance (m)	Replicate	TRC † (mg/L as Cl2)	mean TRC concentration (mg/L as Cl2)	standard deviation (mg/L)	coefficient of variation (%)
3	3	1	0.063			
3	3	2	0.055	0.059	0.006	10.1
3	3	3	-			
3	6	1	0.123			
3	6	2	0.113			
3	6	3	0.102	0.113	0.011	9.4
3	9	1	0.093			
3	9	2	0.084			
3	9	3	0.093	0.090	0.005	5.7
3	12	1	0.086			
3	12	2	0.089			
3	12	3	0.089	0.088	0.001	1.5
3	15	1	0.066			
3	15	2	0.053			
3	15	3	0.060	0.060	0.007	11.1
3	18	1	0.043			
3	18	2	0.064			
3	18	3	0.051	0.053	0.010	19.4
3	21	1	0.035			
3	21	2	0.037			
3	21	3	0.040	0.037	0.002	6.1
3	24	1	0.029	0.029		
3	24	2	ldl			
3	24	3	-			
4	3	1	0.047			
4	3	2	0.048			
4	3	3	0.044	0.047	0.002	4.2
4	6	1	0.046			
4	6	2	0.049			
4	6	3	0.043	0.046	0.003	6.3
4	9	1	0.042			
4	9	2	0.049	0.045	0.005	10.3
4	9	3	-			
4	12	1	0.031			
4	12	2	0.028			
4	12	3	0.041	0.033	0.007	20.8
4	15	1	0.041			
4	15	2	0.039			
4	15	3	0.039	0.040	0.001	3.6
4	18	1	0.033			
4	18	2	0.038			
4	18	3	0.034	0.035	0.003	7.2
4	21	1	0.033			
4	21	2	0.033			
4	21	3	0.031	0.032	0.001	2.8
4	24	1	0.023			
4	24	2	0.034			
4	24	3	0.033	0.030	0.006	20.4
4	30	1	0.019			
4	30	2	0.021			
4	30	3	0.019	0.020	0.001	6.8

Table E2 con't

Cross Section	Transverse Distance (m)	Replicate	TRC † (mg/L as Cl2)	mean TRC concentration (mg/L as Cl2)	standard deviation (mg/L)	coefficient of variation (%)
Night sampling results						
3	6	1	0.124			
3	6	2	0.117	0.121	0.005	3.9
3	12	1	0.129			
3	12	2	0.129	0.129	0.000	0.0
4	3	1	0.051			
4	3	2	0.048	0.049	0.002	4.8
4	12	1	0.042			
4	12	2	0.043	0.043	0.001	1.5
4	18	1	0.031			
4	18	2	0.031	0.031	0.000	0.0

† ldl - less than detection limit

Appendix F

Chlorine plume microbial data

Table F1 Microbial data from Rossdale chlorine plume.

Cross section	Transverse distance (m)	Total heterotrophs (CFU/100 mL)	Total coliforms (CFU/100 mL)	Fecal coliforms (CFU/100 mL)
upstream	3	3670	13500	10
	10	6130	20000	13
	30	5470	28900	263
outfall	09:30 a.m.	22	3	<1
	11:50 a.m.	17	7	<1
1	3	2080	3433	30
	10	1290	4100	9
	12.5	763	5570	35
1A	3	875	3030	7
	6	873	7700	10
	12	1410	12800	52
	18	1010	16500	84
2	2.5	943	6370	29
	10	947	3370	5
	15	967	2630	5
	15	863	6270	15
	18	817	6870	15
3	3	1900	11700	19
	6	1784	20900	43
	9	2340	22730	147
	12	1187	20000	63
	14	1345	28000	28
	18	1700	28600	20
4	3	1100	11700	19

Table F2 Microbial data from E.L. Smith chlorine plume.

Cross section	Transverse distance (m)	Total heterotrophs (CFU/100 mL)	% as coloured flora	Total coliforms (CFU/100 mL)	Fecal coliforms (CFU/100 mL)
upstream	0.25W	158	28	339	53
	0.5W	154	25	518	21
	0.75W	107	18	320	4
	1.0W	145	33	345	4
outfall		2	0	< 1	< 1
1	3	2	0	3	< 1
	6	6	50	11	< 1
	9	13	38	< 1	< 1
	12	44	16	< 1	< 1
	15	30	27	< 1	< 1
	18	27	11	75	4
	21	68	19	329	72
2	3	37	22	12	< 1
	6	54	9	< 1	< 1
	9	88	38	70	20
	12	83	23	112	16
	15	184	40	429	20
	18	214	10	491	67
3	3	77	17	285	8
	6	146	34	285	121
	12	116	39	222	20
	15	40	18	248	23
	21	78	26	299	29
	24	82	17	316	24
4	3	60	28	421	29
	6	124	30	339	580
	9	140	26	342	358
	12	79	35	366	67
	15	51	22	326	62
	18	40	28	367	50
	21	43	23	312	152
	24	82	18	396	138
	30	68	29	392	177